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Heavy Metal Pollution from Spillage at Ore Smelters and Mills

Calspan Corp, Buffalo, N Y Environmental Systems Dept

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Industrial Environmental Research Lab -Cincinnati, Ohio

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16. ABSTRACT

Smelter and mill wastewater outfalls, receiving water, biota, slag heaps, tailings ponds, streams, and coal-burning fly ash dumps were sampled as part of this effort to determine the effect of effluent or residual spillage on aquatic systems. Since concentration of heavy metals in sediment was found to be greater at any given time than that dissolved in water, flood water erosion of particulate matter presents a hazard. Up to 17% lead, 0.1% cadmium and 5 ppm thallium were found in sediments of streams used for irrigation and drinking water below copper and zinc extractive industries in high runoff regions.

Groundwater infiltration in the Northwest and Ozarks provides mine drainage water which is used as process water in mills. This water transports potentially toxic wastes into naturally erosive bottom sediments thereby contaminating the food chain. Heavy metal concentrations in water and biota tend to be higher in the fall at low water following benthic accumulations during the growing season.

Prevention techniques recommended here include separation of waste streams, protection of tailings dams from flood erosion, and recycle of mill and smelter wastewater. Excess water discharged can be treated with lime at elevated pH to precipitate heavy metals and to prevent leaching of sediment already in streams.

The overall sensitivity achieved for thallium by a method developed and reported here is 0.1 ppb in water. The detection limit for thallium in biota was determined to be approximately 10 ppb and 80 to 90 ppb in sediment. This was due primarily to the presence of high concentrations of chloride and other interfering ions in the collected samples.

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HEAVY METAL POLLUTION FROM SPILLAGE AT ORE SMELTERS AND MILLS

by

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Calspan Corporation
Buffalo, New York 14221

Contract No. 68-01-0726

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution-control methods be used. The Industrial Environmental Research Laboratory--Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

Thallium, lead, copper, cadmium, indium, and zinc were determined in streams, sediment, biota, and land at twenty-five sites. The heavy metals are introduced partly during operations as effluents (water or particulates) and partly as spillage during leaching, runoff, dike failure, etc. The work was specifically undertaken to determine whether the thallium solubilized in ore processing was, like mercury, finding its way into the food chain. The problem is not as severe as anticipated, and proper housekeeping and treatment of waste water with lime can significantly reduce the problem that does exist. The results complement other work on air and land pollution that results from smelting. The report will be of interest to those concerned with the uptake, effect, and distribution of trace metals, and to health authorities who need data on the level of toxic metals in mill towns near smelters. For further information contact the Resource Extraction and Handling Division.

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Director
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Cincinnati

ABSTRACT

Smelter and mill wastewater outfalls, receiving water, biota, slag heaps, tailings ponds, streams, and coal-burning fly ash dumps were sampled as part of this effort to determine the effect of effluent or residual spillage on aquatic systems. Since concentration of heavy metals in sediment was found to be greater at any given time than that dissolved in water, flood water erosion of particulate matter presents a hazard. Up to 17% lead, 0.1% cadmium and 5 ppm thallium were found in sediments of streams used for irrigation and drinking water below copper and zinc extractive industries in high runoff regions.

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The overall sensitivity achieved for thallium by a method developed and reported here is 0.1 ppb in water. The detection limit for thallium in biota was determined to be approximately 10 ppb and 80 to 90 ppb in sediment. This was due primarily to the presence of high concentrations of chloride and other interfering ions in the collected samples.

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SECTION I

INTRODUCTION

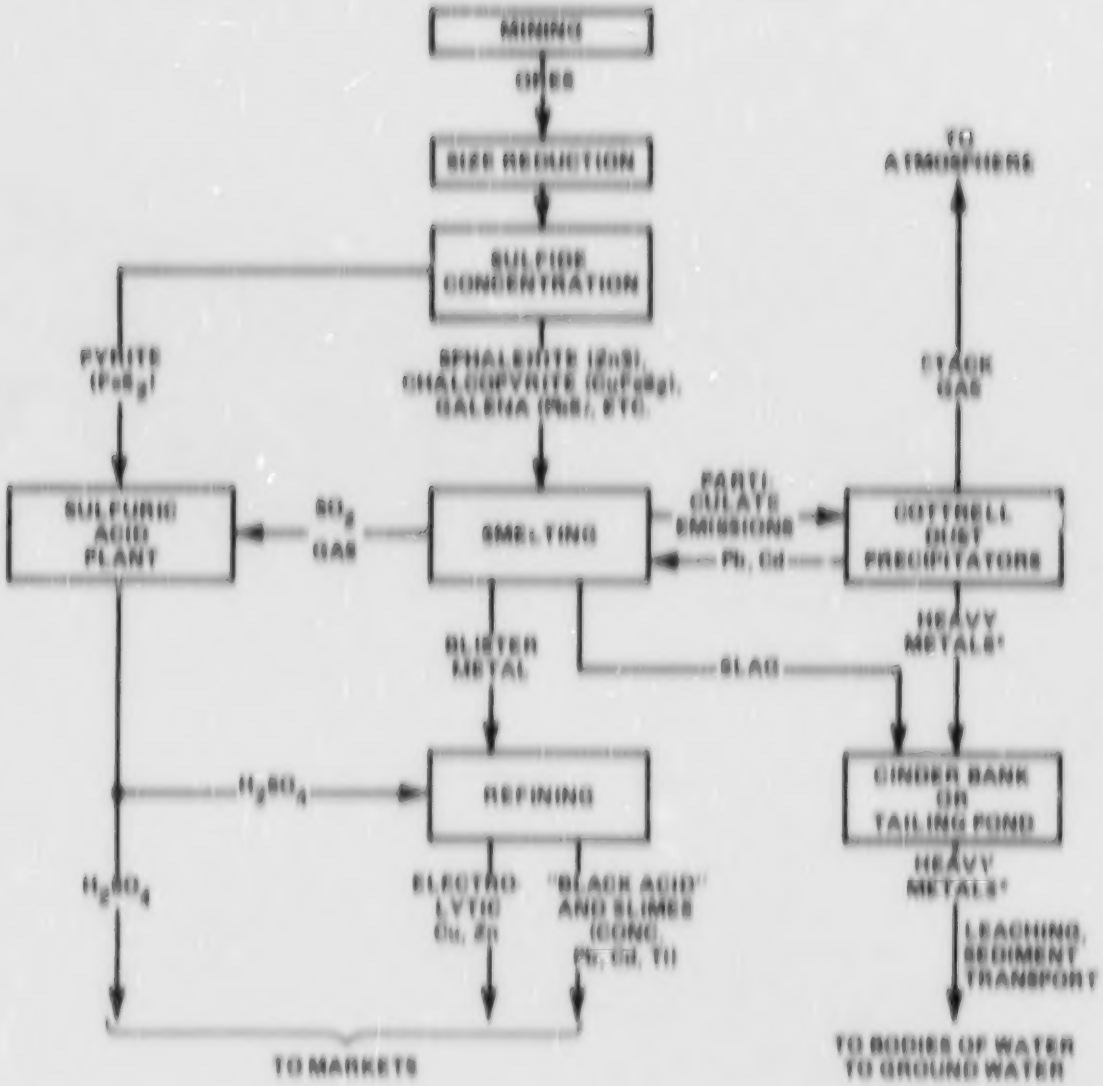
Toxic metals are widely distributed in their natural state. Traces of these compounds are found in a wide variety of rocks and fuels, and commonly occur in association with ores of commercial importance, such as the ores of copper, lead, and zinc. One such group of toxic metal compounds involves the element, thallium (Tl).

Actual production and use of thallium in the United States is small: 6,000 to 7,000 pounds per year (in 1973). Since the demand for Tl is limited by its toxicity and price, the American Smelting & Refining Company (ASARCO) supplied the domestic market from its Denver, Colorado, cadmium smelter. Other Tl concentrates are dumped on cinder banks and into tailing ponds where they present a potential pollution hazard.

Commercially, the small amount of thallium produced is recovered from the cadmium-bearing flue dusts of zinc smelting operations. Most of these flue dusts are returned to the smelter but may be stored in waste cinder banks, which are thus a source of pollution due to the leaching action of rainwater upon the soluble thallium salts present, or to erosion of the waste banks. Thallium pollution may also result from the sudden discharge of residues and spillage of waste liquors from a variety of refining and chemical operations, including lead and copper refining, sulfuric acid and pigment manufacture, and almost all fuel-burning processes. Additional damage to the aquatic environment may also result from accidental spills during the manufacture, transport, storage, and use of commercially produced thallium and its compounds. The toxic compounds of other metals such as copper (Cu), cadmium (Cd), lead (Pb), zinc (Zn), arsenic (As), indium (In), and selenium (Se), which are related to, or associated with, thallium-bearing ores, are concentrated in similar waste deposits and can also pollute the aquatic environment.

Tl tends to be concentrated in the tailings, waste liquors, and dusts of smelters, refineries, and pigment plants using sphalerite (ZnS), galena (PbS), and chalcopyrite ($CuFeS_2$), which are processed in the greatest quantities.

Figure 1 is a chart showing the flow of thallium and related heavy metals from mines to disposal areas and their suspected entry into aquatic environments.



*Tl, Pb, Zn, Cd, In, As, Se, Te, and Cu

Figure 1. Generalized flow chart showing industrial pathway of thallium and related heavy metals and their transport to aquatic environments.

A comprehensive program was conducted to determine the occurrence and movement of thallium and related toxic metals from ore refining and chemical operations to water bodies. This involved sampling and chemical analysis of water sediments and biota from all possible sources and sinks at a site. Sources included slag piles, cinder banks, land fills, and effluent discharges.

Primary sinks include the water and sediments of receiving water bodies and ground water. Aquatic biota serve as secondary sinks for thallium and related metals by uptake, first as dissolved or complexed ions and later by passage through food webs. The hydrology of the disposal areas was of critical interest. Field examinations indicated the potential pattern of runoff and erosion.

The sampling program was planned and carried out to elucidate the extent of movement and concentration of thallium and related metals in physical and biological compartments of the aquatic environment. The potential magnification of heavy metal concentration through the food chain has been carefully investigated at contaminated sites, clean control sites, and in the laboratory.

SECTION 2

SUMMARY

Samples of water, sediment, soil, and biota (algae, larvae, nymphs, fish, rushes, reeds, etc.) were collected and analyzed. The samples were taken from over 50 sites (operations) in 11 major regions of the United States where copper, lead, and zinc are mined, milled, smelted, and refined. The purpose of this sampling and analysis project was to determine the potential for unrecovered (residual) spillage and leaching of thallium and related heavy metals (Cu, Cd, Pb, Zn, and In) from cinder banks, tailings ponds, and slag heaps associated with these operations. Also sampled were a few coal-burning plants and chemical works (i.e., the effects of leaching of flyash dumps and of toxic stack emissions upon the environment were noted). The vulnerability of protective works (if any) for given volumes of toxic wastes is estimated for each site.

The inland smelters and mills surveyed generally had extensive slag heaps and tailing ponds along streams for waste disposal; estuarine and riparian ore-refining facilities generally dispose of wastes directly into water bodies through outfalls. Though some operations continuously discharge very contaminated water, the greatest hazard is erosion of particulate matter in stored wastes by floodwaters.

The concentration of any of the metals was greater in moving sediment at any time than that dissolved in water. Concentrations in water and biota were higher in the fall at low water following benthic accumulations during the growing season. Some bioaccumulation was observed but the data are incomplete, and inconsistent since it was generally not possible to obtain representative samples of appropriate trophic levels in the food chain.

The pollution hazard from toxic metals is greatest in tailings, slag, and the mud eroded from them. Up to 17% lead, 0.1% cadmium, and 5 ppm thallium were found in the sediments of streams used for irrigation and drinking water below copper- and zinc-extractive industries in high-runoff regions, particularly in the vicinities of East Helena and Anaconda-Butte, Montana; Kellogg, Idaho; and Tacoma, Washington. Smaller amounts of these toxic metals are present in effluent waters and biota below the above sites, at open-pit copper mines on Mineral Creek and elsewhere in Arizona, on Whitewater Creek, New Mexico, and at the new lead mills and smelters in Missouri.

Groundwater infiltration in the Northwest and the Ozarks provides mine drainage water which is used in mill or concentrator tailings transport, slag granulation, and refinery sludge disposal. This large volume of water transports toxic waste into naturally fluvially erosive bottom sediments, thereby contaminating the food chain.

Lead and cadmium were also found to be leaching into streams from flyash dumps from a power plant in East Corning, New York.

Prevention of hazardous spills can include proper construction of retaining dams and recycling of mill and smelter water with separation of excess mine water to reduce the amount to be evaporated or recycled. Treatment methods include alkaline precipitation with lime at pH as high as 12 to prevent leaching of toxic metals from polluted mud already in streams (now being achieved in Silver Bow Creek at Butte). Precipitation with sulfide for economic recovery of metals offers potential for ultimate control.

Procedures for determing thallium by atomic absorption in the presence of high concentrations of chloride and other ions were developed. The overall sensitivity achieved for thallium is approximately 0.1 ppb in water. The detection limit for thallium in biota is typically 10 ppb and in sediment 80 to 90 ppb because of interferences present in any samples. Metal uptake (Tl, Cu, Zn, Cd, Pb) by algae was measured in the laboratory. Experiments showed that dissolved thallium ions in water can exchange with ions (probably potassium) in clay; this mechanism can explain the relatively low concentration of thallium in fresh and sea water compared the much higher concentration in river sediment and in the earth's crust.

SECTION 5

CONCLUSIONS

Based on samples and data collected in 1973 and 1974, the following conclusions are drawn.

High levels of toxic metals were found in the particulate matter discharged from northwestern mills, smelters, and refineries, especially from older smelters such as those in East Helena, Montana. Levels were lower in the New Lead Belt in Missouri and very low at White Pine, Michigan, on Lake Superior. Fine, granulated slag and tailings have a large surface area for leaching and are subject to catastrophic erosion.

Hazardous concentrations of over 15 ppm Tl, 1% Pb, and 0.1% Cd have been found in stream sediments below metal sulfide processing facilities (Table 1).

Data from the study show a definite tendency for heavy metals to accumulate in rooted plants in greater concentrations than in algae, fish, or other biota.

The estuarine plants and refineries, and those riparian plants and refineries on large rivers were the most serious polluters since they dispose of wastes directly into the water body through outfalls. Smelters and mills (concentrators) have extensive cinder banks and tailing ponds along the rivers. The greatest potential threat is transport of particulate matter by floodwater.

In general, the volume of toxic metal in the moving sediment of the streams is much greater than the amount in the water at any given time. There is little observable bioconcentration through food chains as compared to sediment concentration of the more toxic metals, especially thallium.

Since the thallium is tied up in the sediments and very little of the sediments from the smelters or natural thalliferous occurrences reaches the oceans, the low concentration of thallium in the oceans as compared with the concentration in freshwater runoff is believed to be associated with the reduction of the thallic to the thallous ion, with substitutions of the latter for potassium in clays.

Indium was rarely found above background but was concentrated enough to report for Tacoma (Table 8) and Kellogg (Table 9).

TABLE 1. THALLIUM CONCENTRATIONS (ppm)

Biota	
Kellogg, Idaho, Bunker Hill copper smelter, horsetail roots under stack	2.8
Kellogg, Idaho, S. Fork of Coeur d'Alene River, crenafly in water	1.8
East Helena, Montana, Prickly Pear Creek, cattail roots in smelter pond	1.0
Tacoma, Washington, ASARCO copper smelter/refinery, horsetail leaves under stack	0.77
Kellogg, Idaho, S. Fork of Coeur d'Alene River, grass roots in water	0.59
Kellogg, Idaho, Bunker Hill copper smelter, horsetail leaves under stack	0.5
East Helena, Montana, ASARCO zinc smelter runoff, Spirogyra	0.48
Anaconda, Montana, Warm Springs Creek, stonefly larvae below old mines	0.45
Tacoma, Washington, Point Defiance, Ulva on beach at ASARCO copper smelter/refinery	0.28
Tacoma, Washington, horsetail roots on beach at ASARCO copper smelter/refinery	0.22
East Helena, Montana, Prickly Pear Creek, cattail leaves	0.083
Kellogg, Idaho, S. Fork of Coeur d'Alene River, Spirogyra	0.061
East Helena, Montana, Prickly Pear Creek, slime on diatomaceous Spirogyra	0.012
Water	
Kellogg, Idaho:	
Slag runoff after leaching	0.11
Mill outfall	0.02
Granulating water	0.016
Sediment	
Kellogg, Idaho, mud	> 10
Butte, Montana, Silver Bow Creek, crust below Anaconda mill	> 10
Tacoma, Washington, ASARCO copper smelter/refinery, slag with live prawns	9.1
East Helena, Montana, ASARCO zinc smelter, septic ooze	6.6
Kellogg, Idaho, S. Fork Coeur d'Alene River, mud below slag and outfalls	4.8
Kellogg, Idaho, Bunker Hill zinc plant, Government Gulch	1.7
Kellogg, Idaho, Bunker Hill copper smelter, soil under stack	1.1
Butte, Montana, Silver Bow Creek, bottom soil below Anaconda mill	0.61
Butte, Montana, Silver Bow Creek, mud below Anaconda mill	0.52
Basin, Montana, mud from ruined mill	0.44
Kellogg, Idaho, Government Gulch, mud below Bunker Hill zinc plant	0.42
Selby, California, ASARCO lead smelter, soil under stack	0.32

SECTION 4

RECOMMENDATIONS

The following recommendations are offered:

Greater care and, perhaps, closer inspection should be expended in the proper construction and maintenance of retaining dams.

Water should be recycled wherever possible--not just where water is scarce or expensive.

Treatment of any discharged water with hydroxide neutralization or precipitation and sulfide precipitation can be used to reduce metal concentrations of effluent waters. (Although the effluent may be more alkaline than ideal, it will also be less toxic. Alkalinity can be reduced by recarbonation.)

Close surveillance of sulfide ore-concentrating processes should be implemented by mill owners in humid regions where floods and excess water process occur--particularly, where dams are constructed only of tailings.

Separation of low pH mine drainage waters from mill wastes should be accomplished where possible to reduce the volume of mine water in contact with tailings. Where this may not be feasible, neutralization of mine waters prior to mixing of waste streams should be considered.

Slag granulation should be avoided, where possible, since it enhances metal leaching due to the exposure of more surface area. However, recycling of slag granulation water should be practiced to minimize cooling water volume and contamination of surface or ground waters by discharge.

Further field studies and analyses are needed to define the industrial toxic metal threat more precisely--particularly, on more generally polluted rivers such as the Ohio, Illinois, and Raritan.

SECTION 5

APPROACH

SITE SELECTION

Sites to be sampled were selected from those refining and chemical operations which produce residues and waste liquors containing toxic metal compounds. They included smelters and metal refineries, a steel mill, sulfuric acid plants, a pigment (lithopone) plant, and fuel-burning power plants in close proximity to watercourses.

Selected sites were sampled in sufficient detail to provide a picture of the course of pollution by thallium (Tl) and associated heavy metals into and through the aquatic environment. Representative operations which discharge into relatively clean fluvial and estuarine waters were selected. Those streams with significant downstream human ultimate consumption were emphasized.

Sites selected for sampling are listed in Table 2. As indicated therein, plants operated by some or formerly operated by firms were sampled in over 30 geographic regions. In many regions, several operations managed by the same firm were sampled, so samples were collected (and analyzed) at considerably more than 30 sites. In addition, several types of samples were collected at most sites.

The locations of all sites sampled are shown on an index map (Figure 3).

The list of Table 2 does not include scrap smelters, because their starting material contains much less heavy metals than the sites selected, and significant concentrations of these metals should be quite rare at such smelters. The plants listed in Table 2 are near water bodies used by large populations. All of the significant sites drain directly into water bodies.

Copper and lead/zinc sulfide ore milling, smelting, and refining produce the bulk of the heavy-metals pollution problem. Although it was not possible to test all such facilities operating in this country with the funds available, the sites selected are believed typical or worse relative to operating procedures for waste disposal and are situated on streams of ecologic significance.

In the processing sequence from sulfide ore to metal product, mining creates coarse dumps which can leach slowly and be eroded by streams. Milling produces large quantities of fine tailings which can be leached

TABLE 2. SITES STUDIED

Site	Description	Comments
Western U.S.		
Tacoma, Washington	ASARCO, Inc. (Asarco Smelting & Ref Leg Co.) Cu/Ag smelter[1], refinery	Tacoma Asarco tailings; Dia Puget Sound
Kellogg, Idaho (Coeur d'Alene)	Bunker Hill et al. Pb/Zn/Cd/Cu/Sb/Fe/Ag/Au smelter[1], mills, mines	Tacoma Asarco / slags into Harbor @ Ruston Point
East Helena, Montana	ASARCO, Inc., Pb/Cu/Ag/Au smelter, Zn slag fuming	Tacoma Asarco drains into Missouri River via Prickly Pear Creek
Basin, Montana	(Abandoned and inactive) smelter, mill	Upper Red Mining in Boulder River
Butte/Anaconda, Montana	Defunct (Cu) smelter & Berkeley (Cu/Zn/Pb/Ag/Au) mill Anaconda (Cu) smelter[1], mills, mines	Lime pit at Butte; mines drain at Anaconda Drains into Clark Fork of Columbia River
Selby, California	ASARCO, Inc., Pb/Zn smelter[1]	On San Francisco Bay; closed
Southwestern U.S.		
Hayden/Riiz, Arizona	Kennecott Copper (proposed) Cu smelter[1], mill, mine ASARCO, Inc., Cu/Ag/Au smelter[1], mills, mines	Being studied by U.S. Hydrosol; Drains into Gila River
Miami/Globe, Arizona	Magma Copper Co. Cu-Mo smelter, mill, mine	Drains into San Pedro River
Globe/Miami/Kearney, Arizona	AMAX, Inc. (American Metal Climax, Inc.) Mo plants Kennecott Copper Co. Cu smelter[1], mill, mine Magma Copper Co. Cu mine, mill	Eventually drains into Salt River
Hayden, Arizona	Phelps Dodge Corporation Cu smelter[1], mill, mine	Drains into Gila River via tributaries
Fierro, New Mexico	U.V. Industries, Inc., Cu/Fe/Pb mills, mines	Eventually drains into Mimbres River
Deming/Hurley, New Mexico	Kennecott Copper Corp. Cu/Mo smelter[1], mill, mine ASARCO, Inc. Cu/Pb/Zn/Ag mine	Drains into streams used for irrigation
Tyrone, New Mexico	Phelps Dodge Corporation Cu/Ag/Au mill, mine	Eventually drains into Mimbres River
El Paso, Texas	ASARCO, Inc., Cu/Pb smelter[1], Zn slag fuming	Drains into Rio Grande
Hayden Mine (Harker), Arizona	Powdered Metals Corporation Cu mine	Closed; drains into Colorado River
Midwestern U.S.		
Viburnum, Missouri	St. Joe Minerals Corp. Pb/Zn/Cu mill, mines	Being studied by U.S. Bureau of Mines; drains into Mississippi River via Big River and streams
Bixby/Fegley, Missouri	Mine La Motte (Mo. Lead Opening Co.) Bunker Pb/Zn smelter[1], mill, mines Combined American, Inc., Magnesium Pb/Fe/Fe/Ag mill, mines	Drains into Mississippi River via creeks and Meramec River and into Black River
Bonne Terre/Fegley, Missouri	St. Joe Minerals Corp., Flotation Pb/Zn/Cu mill, mines Kennecott Copper Corp., Doe Run Lead Co.) Pb/Zn mill, mines	Drains into Black River via creeks
Fredericktown, Missouri	St. Joe Minerals Corp., Federal Bureau Pb/Zn mill, mines	Standby; drains into Fast River
Glover, Missouri	ASARCO, Inc., Pb smelter	Some drainage into Big Creek; mines reclaimed
Herculaneum, Missouri	St. Joe Minerals Corp., Pb/Fe/Ag smelter[1], refinery	On Mississippi River
East St. Louis (Granite), Illinois	AMAX, Inc., slag/Cu-bytes Zn/Pb refinery[1]	On Mississippi River flood plain
White Pine, Michigan	Copper Range Co. Cu smelter, mill, mine	On creeks draining into Lake Superior
Eastern U.S.		
Perth Amboy, New Jersey	ASARCO, Inc., Cu/Ag plant, Amo refinery Anaconda Co. Cu/Au/Ag/Au electrolytic refinery	Drains into Arthur Kill, Raritan River, and Raritan Bay
Sayreville, New Jersey	Chemical Pigments and Chemical Works, Inc., pigment plant	
Palmerton, Pennsylvania	The New Jersey Zinc Co., Pb/Zn/Cd smelter[1], refinery	Drains into Lehigh River via creek
Other Known Thallium-Bearing Activities/Areas		
Salt Lake City Region, Utah[2]	Mid-Continent & Ruberoid Roofing Products Co. Pb/Zn/Ag/Au mine (Bingo)	Mine complex drains into Bingo Salt Lake
Mercury, Utah[2]	Manufacturer and Chemical Works Co. Zn smelter	Non-operating; drains into Utah Lake
Sperry, W. Virginia[2]	ASARCO, Inc., (Mountain plant)[2]	No longer in use; mine now abandoned
Fairmount, Ohio[2]	Bethlehem Steel Corporation coke mill[2]	Non-operating; ash effluent ponds still
Bethlehem, Pennsylvania	Bethlehem and plants & Cu/Zn/Fe smelter[1], mills, mines	Ash ponds; coke no longer used on Lehigh River
Copper Basin, Tennessee	Ducktown Chemical & Iron Co.	Drainage into Ocoee River
Andrews (Hungarian & Slovenian) Pennsylvania	Pennsylvania Power & Light Co.	Standby or closed; drains into Susquehanna, Schuylkill and Lehigh River
Eagle Rock, New York	Bituminous coal burning power plant	Coal fired; land impacted; ponds; applied ashes to fields prior to sampling; fly ashes/slag

[1] Also includes coal plant. (Boilers and calciners)
[2] Study also not completed. (Response to coal smelting are more fully described in Appendix B.) Locations of all other sites are shown in Figure 2.

Figure 2: Locations of the Monitoring Stations

rapidly. Containment is now attempted for most active mills, although removal by flood erosion still occurs rarely at some large ponds such as at Anaconda, Montana. Smelting, by hot reduction and oxidation, releases metals as air pollution and produces slag, which is leached and washed away.

The effluent metal concentrations are relatively low. The tank house or final electrolytic refining step is often integrated into the smelter complex, as at the Tacoma, Washington, and Kellogg, Idaho, sites, to utilize acid produced from the smelter sulfur oxides. This acid is released (or, sometimes, sold), often without recovery of unsalable byproducts such as thallium and arsenic. The effluent is often reused at integrated plants, so metals are recycled or concentrated at a few final outfalls.

The processing at these older plants is similar to that described in the text of Section 6 on the White Pine, Michigan, site although the operating conditions and ore characteristics vary. In general, the western smelters are larger and farther from byproduct markets. Their ores, formed at higher temperatures, are richer in additional sulfides, selenides, tellurides, and arsenides (such as those of thallium and related metals), which are released during milling and smelting.

Site conditions and analysis results are described in Section 6 in the order in which the sites are given in Table 2. The remainder of this section summarizes sampling, sample preparation, and sample analysis.

SAMPLING PROCEDURES AND TECHNIQUES

Water, sediment, and biota were sampled at each site, taking into account that leaching and other runoff may be dependent upon the action of rain or flood water.

Samples were collected from drainage ditches, outfalls, and storm sewers emanating from or passing through areas where heavy metals from ore smelting or refining might be present. Additional samples were collected from receiving bodies of water. Further sampling, for references purposes, was conducted on upstream portions of the receiving bodies of water so that background levels of thallium and other metal concentrations might be established. These background levels were needed to confirm whether or not thallium and other toxic metal concentrations in water bodies suspected of contamination from the ore-smelting/refining operation are significantly greater than normal background levels.

Glass bottles were used for sampling water from outfalls, ditches and storm sewers, and shallow receiving streams. Deep bottom water was collected using a Kemmerer bottle. Because the solubility of most metal compounds is low, it was expected that water concentrations would often be in the parts-per-billion range. Therefore, sufficient volumes were collected for each sample to ensure adequate quantities for those samples which might require repeated chemical analyses. The minimum volume of water collected was 200 ml. Collected water samples were shipped in their glass collection

bottles, and samples obtained using the Kemmerer bottle were placed in glass bottles for shipment.

Sediment samples were placed in small 25 ml glass containers with polyethylene tops which were pre-weighed and initially labeled at the laboratory prior to each trip.

Suspended sediments were separated from water in the field and analyzed separately. Collected bed-load sediments were elutriated to separate silt and clay-sized particles from sand. These fractions were analyzed separately wherever possible.

Collection and chemical analysis of receiving-water biota were conducted to determine the extent to which thallium and associated heavy metals accumulate in biota as a result of effluent attributable to ore refining and chemical operations.

Specific aquatic food-web species were sampled (and analyzed) according to the type of water body, geographical location, and degree of pollution. Particular attention was given to sampling at various trophic levels in food webs to ascertain whether or not bioconcentration of metals occurs through food chains. Figure 3 is a generalized food web for a stream community consisting of a number of interrelated food chains. The food-web diagram suggests the degree of complexity involved among the various food chains or building blocks of the web. The lines connect trophic levels and represent the "upward" movement of food material through the diagrammatic community.

Of the two most important organic-matter inputs to the food web--namely, detritus and stream drift--the former was sampled to determine pollutant inputs via this route. The stream producers (first trophic level) such as algae were also sampled, as this trophic level is a major point at which pollutants are incorporated into living tissue. Proceeding further up the food chain, samples were collected of many primary-consumer benthic organisms (such as insect nymphs and larvae, snails, mussels and clams, and oligochaete worms), which feed principally from the imported organic matter (detritus), algae, and diatoms. Toward the top of the food web, predaceous insects and fish were sampled, as well as omnivorous organisms such as suckers, which occupy an intermediate position between the two major consumer trophic levels.

The food web shown in Figure 3 is a generalized composite, and genera and families/orders have been cited for their traditionally accepted trophic roles. The food web shown applies to a community in a relatively unpolluted environment; however, the food webs for streams and estuaries where some metal refineries are located do not resemble that shown. One stream receiving refinery wastewater, the South Fork of the Coeur d'Alene River at Kellogg, Idaho, was found to contain only pollutant-tolerant organisms, such as sludge worms and midge larvae.

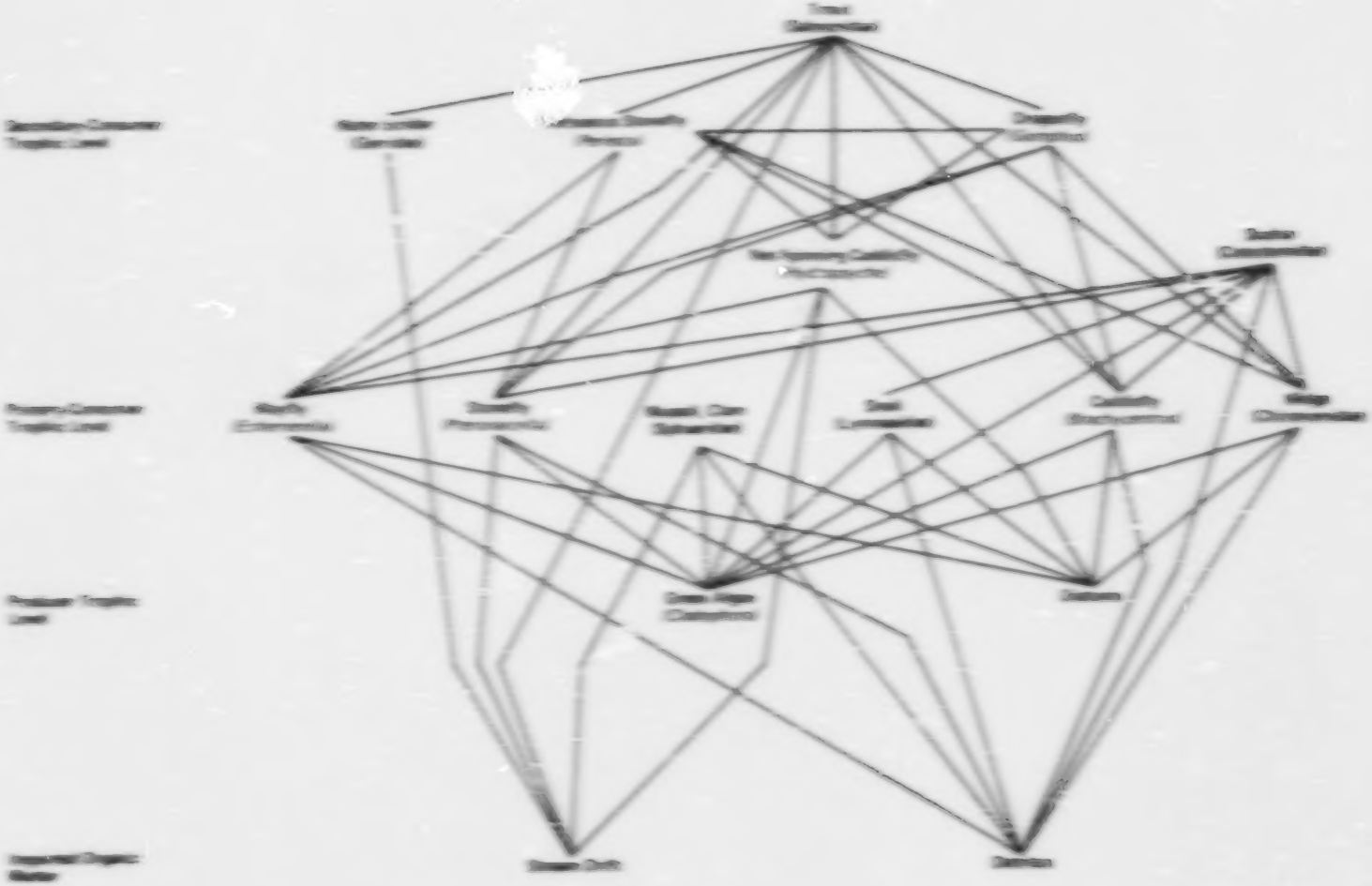


Figure 2. Conceptual food web for a village community

Equipment used for biological sampling included dip nets, plankton nets, drift nets, and an Ekman dredge and Kemmerer bottles for bulk sampling of water-dwelling organisms. Biota samples were placed in glass containers which varied in capacity according to the size requirements of the collected specimen. Guidance on sampling, sorting, and preservation of biological samples was provided by appropriate EPA personnel.

Analytical controls (blanks) composed of distilled water in 200 ml glass jars were carried into the field. Blanks showed less than 10 ppb zinc, 20 ppb copper, 30 ppb cadmium, 10 ppb lead, 100 ppb indium, and 0.1 ppb thallium.

After completion of sampling at a particular site, preserved samples were packed and shipped to the Calspan laboratory as part of the on-flight baggage of the field-sampling personnel. On-site preservation of the water samples consisted of the addition of 1.0 ml of concentrated nitric acid per 200 ml sample to stabilize metal concentrations. Biota samples were preserved with formaldehyde solution at concentrations appropriate to the physical size and physiological nature of the collected specimen. No initial preservation of solid sediment samples was required or deemed necessary.

SAMPLE PREPARATION

Water samples were analyzed by direct aspiration after settling of any particulate matter. The majority of those samples were also extracted with diethyldithiocarbamate (DDC) and 4-methyl-2-pentanone (MIBK) to concentrate thallium prior to analysis.

The bulk of the sediment samples were analyzed for available metals. Since the moisture content of the samples as collected varied widely, 2-gram portions were dried and weighed prior to extraction. Extraction was by a 24-hour exposure of 2 grams of the sample to 2 ml of a 1:1 mixture of concentrated nitric and hydrochloric acids at room temperature (20°C, 68°F). The acid solution was diluted to exactly 20 ml with distilled water prior to analysis. Metal content was reported on a dry-weight basis.

This method was chosen after preliminary investigations were conducted to determine the most efficient method for leaching metals from sediment samples. Further information on the study and rationale for the selection of this method is provided in Appendix A.

Biological sample analysis was performed on a wet-weight basis, with excess (surface) moisture removed at the sampling location. Digestion was performed in the collection bottles to avoid loss of material and contamination of samples. Sample weight was obtained by subtracting the predetermined bottle weight from the weight of bottle with sample. A 7:3 mixture of concentrated nitric and perchloric acids was then added to the sample on the basis of 1 ml per gram of sample. Digestion was accomplished with the

bottle sealed and placed in a water bath at 50°C (122°F) for 24 hours. The acid solution was then diluted 5:1 with distilled water for analysis.

It was found necessary to concentrate and remove potential interferences from many of the samples prior to analysis. Extremely low-level metal samples and those with interfering ions (sodium and calcium) required a cleanup concentration with DDC chelation, followed by MIBK extraction to separate metals of interest prior to analysis. This was specifically performed to improve the detection and reliability of analysis of the extremely low-level concentrations of thallium encountered. Table 3 describes the DDC/MIBK complexation method for thallium analysis.

TABLE 3. ORGANIC COMPLEXATION METHOD FOR THALLIUM

A. The following reagents are prepared:

1. Diethyldithiocarbamate (DDC) – Twenty grams (309 grains) of diethyldithiocarbamic acid sodium salt are mixed with 900 ml of distilled water. This solution is filtered through a 0.45 micrometer filter. The filtrate is extracted twice with 10 ml portions of MIBK.

2. MIBK – 4-methyl-2-pentanone (Eastman).

3. Phthalate buffer – 102 grams (1,574 grains) of Baker Reagent grade potassium biphthalate are dissolved in distilled water and diluted to 500 ml. Fourteen ml of 1M HCl are added, and the resulting solution is diluted to 1.0 liter.

4. Sodium hydroxide or hydrochloric acid is added to adjust pH.

B. All glassware must be rinsed with 1:1 HNO_3 containing a small amount of HF, followed by rinsing with distilled water, acetone, and more distilled water.

C. Procedure

1. Dilute a sample aliquot to 100 ml with distilled water.

2. Add 5 ml of buffer and adjust pH to 3.5 ± 0.1.
Add 7.0 ml of DDC solution.
Add 10.0 ml of MIBK.
Shake vigorously for 90 seconds.
Withdraw MIBK layer.
Evaporate MIBK to dryness.
Add 2.5 ml of concentrated HNO_3 + 2.5 ml of distilled water.
Sample is ready for analysis.

Other sample preparation procedures developed, but not used because of inherent difficulties, are given in Appendix A.

SAMPLE ANALYSIS

Atomic-Absorption Analysis

Samples were routinely analyzed for thallium, lead, zinc, copper, and cadmium. Additional metals--namely, tellurium and indium--were analyzed only for specifically selected samples. Arsenic and selenium, frequently associated with the thallium-bearing ores investigated in this program, were not routinely analyzed; because the major thrust of the program was directed toward the detection and quantification of thallium in the environment, priority in the program was placed on this objective.

A Perkin-Elmer Model 303 atomic-absorption spectrophotometer, modified to increase its sensitivity, was used for metal analysis. Improved electronics provides detection limits substantially lower than those of the unmodified instrument for some elements, and direct digital readout in concentration is also available (and was used) to expedite the analyses. The instrument is equipped with a deuterium-arc background corrector, and both a sampling-boat accessory and a heated graphite atomizer (HGA) are available and were used as required. An emission-correction circuit was added to sense the emission resulting from the flame and automatically subtract this signal from the photomultiplier output.

The standard detection limits for metals in aqueous solutions analyzed on this instrument are listed below. (In this tabulation, detection limits for lead and tellurium have been extracted from the 1968 Perkin-Elmer atomic absorption accessories brochure; all other limits are from the Perkin-Elmer Analytical Methods Manual, published in 1968.) As the result of the improvements made, the sensitivities listed below were either met or exceeded for the analyses in this program.

Element	Analytical Method	Detection Limit (ppm)
Copper	Direct Aspiration	0.005
Lead	Sampling Boat	0.001
Zinc	Direct Aspiration	0.002
Cadmium	Direct Aspiration	0.004
Thallium	Heated Graphite Atomizer	0.001
Tellurium	Sampling Boat	0.01
Indium	Direct Aspiration	0.05

The method chosen for atomic-absorption analysis of each metal was that method which would consistently provide data with adequate sensitivity for the metal concentration in an individual sample. Direct aspiration, the method of greatest facility and least time consumption, was utilized in the majority of cases. Analysis by sampling boat was used only for lead and those selected cases where tellurium analysis was desired. The heated graphite atomizer was used only for thallium analysis, since this method provides the optimum sensitivity for thallium concentrations which was necessary to provide meaningful final data.

Many different approaches to obtaining thallium-concentration data for natural samples were attempted throughout the early part of this program. Thallium salts in distilled-water matrices posed no problem analytically, but, in the presence of other elements, it became difficult to perform analyses for low-level concentrations of thallium. Presence of large quantities of alkali and alkaline-earth elements caused definite quenching of thallium signals. The direct-aspiration method for atomic absorption was found unsuitable for those samples where minimal thallium levels were encountered.

Straight (nitric and hydrochloric) acid treatment of water and sediment samples, followed by aspiration by conventional means into the atomic-absorption spectrophotometer, produced varying results. Standard samples containing known concentrations of thallium (as the nitrate) could be analyzed easily, yielding interpretable results and calibration curves. At times, levels of thallium were initially "observed" to be present, but slight changes in burner conditions removed the thallium signal. In each case where a response for thallium was observed, the emissions from other elements also in the sample were extremely high. Ordinarily, such emissions, if at moderate levels, can be compensated for with the emission-correction device. Many of the emissions encountered were beyond the capability of this corrector. Dilution of the sample to reduce emissions resulted in complete removal of the previously observed thallium signal. When a thallium response in a sample is relatively large, a 50% dilution of that sample should produce a proportional decrease in the thallium signal; however, no signal was obtained in these cases. Since direct aspiration of acidified samples left the thallium concentrations doubtful or highly questionable, other modes of sample preparation or analysis-technique modification using atomic absorption were deemed necessary.

A heated graphite atomizer was then used in an attempt to eliminate flame effects and to increase sensitivity for thallium. Standard samples of thallium were introduced into the atomizer and produced sensitivities ten times greater than that sensitivity attainable by aspiration. A series of samples was introduced in the same mode as standards, but no signals were observed. Addition of a standard to a sample resulted in a strongly decreased response, or in a complete quenching of the expected thallium signal. It was found, through subsequent investigation, that sodium and (primarily) chloride ions had a large quenching effect. Chloride is very abundant in nature, and all natural samples contain it to some degree. In addition, some of the samples of interest were highly saline (i.e., sea water).

Additions of silver nitrate to samples, as well as to synthetic standards containing thallium and chloride, precipitated the chloride ion as the silver chloride. However, removal of the silver chloride from the samples did not remove the interference in natural samples. This indicated that other components in the sample were still interfering by some mechanism.

An attempt at isolating thallium from the sample matrix was attempted. Two types of thallium removal were tried: one to precipitate the thallium as the sulfide, and the second to complex and extract the thallium as an organic complex. Both techniques also remove other multivalent metal ions from solution, but ions such as potassium, sodium, chloride, and sulfate are left behind.

If thallium levels were high, the sulfide precipitation method yielded detectable results by aspiration. Aqueous samples could be analysed to a sensitivity of approximately 0.5 ppm Tl. However, to attain the greater sensitivity which was desired, the heated graphite atomizer was used with the sulfide precipitation preparation. This method was tested on two water samples, which were analyzed with and without additions of 1 ppm thallium. Thallium was not detected above 0.1 ppm in either sample, thus indicating a quenching of the thallium signal. For this reason, sulfide precipitation in conjunction with the atomizer was determined to be unsuitable for use in this study. Table A-3 in Appendix A details the sulfide precipitation procedure.

Organic complexation using diethyldithiocarbamate (DDC) and subsequent extraction with 4-methyl-2-pentanone (MIBK) was initially performed on a group of selected samples. Standards of thallium were extracted adequately with an approximately 90% efficiency. These samples were analysed by direct aspiration of the organic solvent. Extracted samples mainly showed minimally detectable and questionable concentration, of, or zero response for, thallium. Thallium deliberately added to samples showed quantitative thallium recovery.

Organic complexes of thallium were also analyzed using the heated graphite atomizer. Strong emissions from the decomposing of the complex prevented proper analysis by this mode. This effect was overcome by evaporating the MIBK, which contained the complex, to dryness and redissolving in concentrated nitric acid, followed by dilution to 5 ml with distilled water. Samples were then injected into the atomizer, operating under the conditions listed below. (Oxidation of the complex with perchloric acid or sulfuric acid, instead of nitric acid, either completely quenched the thallium response or added interferance.)

Program:	4 @ 8 volts
Dry Time:	80 seconds at 105°C (212°F)
Ash Time:	350 seconds at 330°C (626°F)
Atomization:	15 seconds at 2200°C (3992°F)
Sample Size:	10 microliters

The type of samples collected in this study varied greatly in their chemical and physical compositions. This necessitated at least one addition of thallium to each sample analyzed in order to verify extraction efficiency. This was especially important with sediment samples, where overall extraction efficiency was shown to be about 50%. For this reason, an addition of 2.5 micrograms of thallium per 10 ml of sample was made to each water sample, and a blank sample, consisting of 10 ml of distilled water with no thallium addition, was also extracted and analysed. Sediment samples were analysed

after digestion with and without addition of 1.0 microgram of thallium.

The extraction procedure just described was generally time-consuming, and careful control had to be maintained to minimize losses. Under optimized laboratory conditions, as many as 25 samples could be extracted per day by this method.

Typical results of the thallium analyses by the organic-complexation method are provided in Table 4; locations of those samples are given in Table 5.

Electrochemical Analysis

A comparative analysis, for the purpose of verification, was made on two selected water samples by the application of anodic stripping voltammetry. This technique has been employed for ppb-level determination of many heavy metals, including silver, cadmium, indium, lead, thallium, and zinc. The thallous ion gives a strong polarographic wave at -0.475 volt in 1M solutions of potassium nitrate, chloride, sulfate, and hydroxide.

Two water samples from the Kellogg, Idaho, site were run for Tl with anodic stripping voltammetry through the courtesy of Dr. Eric Zink of Environmental Science Associates, Burlington, Massachusetts, manufacturer of the equipment. These samples were chosen because they represented the type of sample being analyzed by atomic absorption in this program. Lead and cadmium were measured simultaneously on 50-microliter aliquots of each sample added to 5 ml of 1N sodium acetate, adjusted to pH 5.5. Copper and thallium were measured using 5-ml aliquots of each sample. These aliquots were evaporated to dryness and taken up in 5 ml of 1N sodium acetate and 0.1 ml of 6M hydrochloric acid. Copper was measured by plating at -0.5 volt, after addition of 0.2 ml ethylene diamine tetraacetic acid of 0.1N (EDTA) solution. Typical results are shown in Table 6. With the exception of copper in the second sample, agreement with the atomic-absorption technique is reasonably close, indicating that the atomic-absorption determinations are fundamentally reliable.

Conclusions

The development of the organic-complexation heated-graphite-atomizer atomic-absorption analysis method for thallium provided an analytical method with consistent reproducibility and a reasonable degree of sensitivity. Overall sensitivity for thallium was shown to be approximately 10 parts per billion (ppb) for a water-sample size of 10 ml. Sediment samples generally showed less recovery of thallium than the water samples. This may have been due to the large amounts of other metals present also complexing with the DDC and reducing the DDC/thallium ratio, thereby leaving the thallium with little DDC available for complexation. The reduced signal may also be attributed to the presence of other extracted metals interfering with thallium in the atomizer.

TABLE 4. TYPICAL RESULTS OF ATOMIC ABSORPTION ANALYSES OF THALLIUM USING ORGANIC COMPLEXATION METHOD

Sample No.	Relative Response of Instrument	Thallium Concentration (ppm or μg/g)
Water Samples		
— (Blank)	0	0
— (0.025 ppm thallium standard)	9.5	0.025
— (0.050 ppm thallium standard)	14	0.050
— (0.125 ppm thallium standard)	24	0.125
— (0.250 ppm thallium standard)	38	0.250
— (0.500 ppm thallium standard)	55	0.500
4L-21	4.0	0.01
4L-21 + 0.25 ppm thallium	33	
4L-26	2.0	< 0.01
4L-26 + 0.25 ppm thallium	39	
6L-5	1.5	< 0.01
6L-5 + 0.25 ppm thallium	38	
6L-10	2.0	< 0.01
6L-10 + 0.25 ppm thallium	37	
6L-15R	3.0	< 0.01
6L-15R + 0.25 ppm thallium	22*	
Sediment Samples		
— (0.5 μg thallium standard)	19	0.5
— (1.0 μg thallium standard)	25	1.0
— (2.0 μg thallium standard)	38	2.0
2-35 (sample weight, 0.1348 g)	1.0	< 2
2-35 + 1.0 μg thallium	15	
3-47 (sample weight, 0.0470 g)	3.5	< 8
3-47 + 1.0 μg thallium	13	
4-5 (sample weight, 0.0166 g)	3.0	< 15
4-5 + 1.0 μg thallium	16	
4-20 (sample weight, 0.1343 g)	8.0	8.6
4-20 + 1.0 μg thallium	15	
6-1 (sample weight, 0.0277 g)	3.5	< 7
6-1 + 1.0 μg thallium	16	

*Very broad peak

TABLE 5. LOCATIONS OF SELECTED SAMPLES ANALYZED FOR THALLIUM BY ORGANIC COMPLEXATION METHOD

Sample No.	Location	Operation	Comments
Water Samples			
4L-21	Kellogg, Idaho	Bunker Hill Co.	Discharge onto large slag heap
4L-26	Tacoma, Washington	ASARCO	Outfall running down shore
6L-9	Bixby, Montana	COMINCO American Magmont Mine/Mill	Water from outfall of tailings
6L-10	Viburnum, Missouri	St. Joe Minerals Corp. Fletcher Mine/Mill	Runoff from tailing ponds
6L-16X	East St. Louis, Illinois	American Zinc Company/AMAX	Lagoon, west of electrolytic refinery
Sediment Samples			
3.35	Butte, Montana	Anaconda Co.	Fine sediment from pipe (Silver Bow Creek)
3.47	East Helena, Montana	ASARCO	Sediment from beneath slag heap
4.6	Butte, Montana	Defense Smelter	Blue crust on slag
4.20	East Helena, Montana	ASARCO	Black undersediment from tributary
5-1	Basin, Montana	(Abandoned)	Mud near remains of old mill and smelter

TABLE 6. RESULTS OF COMPARATIVE ANALYSES OF REPRESENTATIVE WATER SAMPLES FROM KELLOGG, IDAHO

Sample	Metal	Concentration (ppm)	
		Atomic Absorption Analysis[1]	Anodic Stripping Voltammetry
Slag Pile Runoff	Thallium	0.1	0.1
	Cadmium	1.0	0.75
	Copper	0.03	0.028
	Lead	(Not Available)	1.8
Smelter Weir	Thallium	0.02	0.036
	Cadmium	2.2	1.8
	Copper	0.03	0.086
	Lead	6.3	4.1

[1] Thallium was determined using the organic complexation method. Cadmium and copper were determined using direct aspiration, and lead was determined using the sampling boat.

Results of analyses for the biological samples indicated some problems with reproducibility of results. Differences larger than expected were found between the results of eight of 25 pairs of replicate analyses. These differences were probably due to the plugging of the aspiration capillary, and it was subsequently found that they could be eliminated by running samples twice or by more frequent standardization.

The organic-complexation method as it now exists appears to have significant potential as a reliable, consistent method for analysing thallium-metal concentrations in a variety of sample types. Additional work to more accurately define the required experimental conditions may be desirable. Variation in operating parameters (such as pH adjustment, temperature modification, acid addition, and others) may provide increased sensitivity as well as decreased sample preparation time. Continued work with the analysis will undoubtedly result in an optimum level of facility and operator accuracy.

SECTION 6

RESULTS

SCOPE OF SECTION

The material which follows in this section is subdivided into (1) Site Descriptions and Analyses and (2) Ecology of Thallium. The first (and larger) subdivision includes detailed descriptions of each geographic region sampled (selected using the criteria given under Site Selection, Section 5) and the results of analyses of the samples for toxic heavy metals. For each of these regions, a map is provided which shows the locations of all sampling sites in relation to bodies of water; other geographic features; and smelting, milling, mining, and/or other industrial operations discussed in the accompanying text. (The reader is referred to Figure 2, in Section 5, for the overall location of each geographic region sampled.) In most cases, one or more tables presented for each geographic region identify the concentrations (in parts per million = mg/l) of all heavy metals found to be present in each type of sample collected at each sampling site. Note that "none" in these tables indicates that the specified type of sample (e.g., slag, mud, or biota) was not present and, therefore, could not be collected or analysed for the site indicated. (It appears that, in many cases, fish or bottom-dwelling organisms were absent due to either high toxic-metal concentrations or low pH.) Where only a few metals were found present in a few samples taken in a region, results for the region are presented in the text rather than in tables.

The organization of Site Descriptions and Analyses precisely follows the organization of Table 2 (Section 5). Like the table, this material has four subsections (categories)--Western U.S., Southwestern U.S., Midwestern U.S., and Eastern U.S.--that reflect generally similar modes of occurrence (geology) and processing methods for the metals involved, plus a fifth, "other" subsection (category). Subsections are presented in the same order as the categories of Table 2; within each subsection, regions (general sites) are discussed in the same order as listed in Table 2.

The ecology of the heavy metals most commonly found associated with thallium--i.e., copper, lead, zinc, and cadmium--has been studied in detail and is thoroughly described in the scientific literature. However, little information on thallium is available in published form. Therefore, this section concludes with a summary of the Ecology of Thallium which discusses the abundance and distribution of this metal, its behavior in natural waters, results of experiments (performed under this program) demonstrating that common clay can take up thallium to

minimise its movement through the food chain, and the biological concentration of thallium. Four graphs summarize data on bioconcentration of thallium, cadmium, and lead based on analyses of the samples collected in the study program.

SITE DESCRIPTIONS AND ANALYSES

Western U.S.

Tacoma, Washington--

The ASARCO (American Smelting and Refining Company) copper smelter and refinery is on Puget Sound at the mouth of Commencement Bay and the adjacent Dalco Passage between Point Defiance and Vashon Island (Figure 4). The estuary was sampled in September 1972 and resampled in May 1973. Tables 7 and 8 contain the data on thallium and other metals from various locations shown in Figure 4.

Much of the concentrate used is imported from the Philippines and is predominantly enargite ($3Cu_2S.As_2S_5$) with significant gold, silver, and pyrite. In addition, arsenical materials from ASARCO operations at Battle Mountain, Nevada, and El Paso, Texas, are processed. At present, the blister copper produced at Tacoma has the highest concentrations of silver and arsenic, and its lead concentration is exceeded only by the Carteret scrap smelter among U.S. plants. The copper is refined by electrolysis in hot acid. The acid at Tacoma is heated to 63°C (145°F) in Pb tubes and purified in lead-lined cells before discharge into the Sound. The slag is granulated in a stream of water in order to allow it to deposit in deep water.

The plant wastes banks, effluent, and waters as far out as possible were sampled from a boat. Dredgings near the principal outfall yielded only shell fragments of dead marine bivalves (scallops and razor clams) in iron-rich mud to a water depth of 60 meters (200 feet) (approximately 0.8 km (0.5 mile) offshore). Green algae was collected from rocks on-shore adjacent to the acid outfall, and also at a location at the north end of the smelter area growing on one of the older slag deposits which form the entire smelter site. Barnacles (Balanus) were also collected at these same sites. In the tidal littoral zone, barnacles (as plankton filter feeders) live closer to the outfalls than algae.

Gill nets were set adjacent to the acid outfall to the southeast of the smelter. A number of crustacean larvae (Metanauplius) were pulled off the net from shallow water. In addition to the three marine fish previously taken by gill net, a large flounder was caught off the dock. Liver, kidney, and muscle samples were taken. Between sampling periods, the acid outfall had been plugged, and effluent was then diverted through a lime pit, raising the pH slightly, and allowed to seep into the ground. Although an elaborate liquid SO_2 plant financed by the state is under construction, no further work was yet underway on the apparent arsenic or heavy-metal problems which are evident in the data presented in Table 8 for the samples collected in May 1973.

Figure 4. Tacoma, Washington, sampling sites.

TABLE 7. CONCENTRATIONS OF THALLIUM (ppm) AT SELECTED SITES NEAR TACOMA, WASHINGTON (ASARCO COPPER SMELTER/ REFINERY—PUGET SOUND, SEPTEMBER 1972)

Sampling Location	Water	Clam Shells*	Green Algae (Ulva)	Horsetails under Stack
Control	<0.01	<0.48	<0.39	
Potential Sources of Thallium				
Smelter	2.4		0.28	leaves 0.77
Slag	<0.01-2	0.1		roots 0.33

*Heat, abraded carbonate fragments found in toxic mud near acid outfall—(preliminary determination, not reproduced) and control at Point Defiance.

TABLE 8. CONCENTRATIONS OF HEAVY METALS (ppm) AT SITES NEAR TACOMA, WASHINGTON (ASARCO COPPER SMELTER/REFINERY—PUGET SOUND, MAY 1973)

Sampling Location	Thallium	Cadmium	Lead	Copper	Zinc	Indium
Control (pH 8)						
Water	<0.0001	0.003	0.02	0.03	0.27	0.3
Mud	<0.1	0.11	0.26	96	150	—
Algae	<0.008	<2	<11	<5	3.3	0.4
Invertebrates	<0.01	—	—	—	—	—
Fish	—	—	—	—	—	—
Acid Outfall (pH 3.8)						
Water	0.0012	0.04	0.4	0.04	7.2	0.4
Mud	0.52	2.5	2400	2500	6200	40
Algae	<0.007	<1.6	440	440	160	3
Invertebrates	<0.06	<2.5	140	320	190	15
		3.5 (shells)				21 (shells)
Fish (Perch, 197±)	<0.06	0.44	12	19	18	—
Dock Outfall (pH 4.2)						
Water	0.00015	0.015	0.015	0.24	1.1	0.1
Mud	None	None	None	None	None	None
Algae	<0.02	2.6	84	360	110	2
Invertebrates	<0.06	<0.4	<44	98	82	<0.6
Fish (including Flounder)	<0.03	<4	66	10	40	10
			510 (spleen)			
Slag (pH 5)						
Water	0.002	0.004	0.02	0.2	0.28	0.5
Mud	0.31	3.5	1700	3400	6000	38
Algae	None	None	None	None	None	None
Invertebrates	9.1	None	None	None	None	None
Fish	None	None	None	None	None	None

Shells of dead clams pave the muddy bottom in front of the acid discharge. They average 5.5 ppm Cd, 50 ppm Pb, 100 ppm Cu, and 220 ppm Zn; Ti is undetectable.

Only Equisetum, seemingly the most tolerant terrestrial vegetation, grows in the dust beneath the stack. The brown algae, Fucus and Laminaria, were taken along the beach east of Pt. Defiance, as were additional green algae northeast of the smelter. This location, upwind in a strong tide rip, is believed to be relatively free of smelter pollution.

Kellogg, Idaho (Coeur d'Alene District)--

This district has yielded ores worth well over a billion dollars in lead, zinc, copper, and silver since 1879. The mines occur within an area about 40 km (25 miles) long and 24 km (15 miles) wide. The country rocks consist of Pre-Cambrian Pritchard black shale, 4 km (2.5 miles) thick, which has been intruded by monzonite very similar to the Boulder granodiorite of Montana. The most productive mines (Sunshine and Bunker Hill) are found along great faults continuing east into Montana; the Osborn fault has a vertical displacement of 5 km (3 miles) or more and a horizontal displacement measured in tens of miles. Between these great faults are minor faults and shear zones that have been filled and replaced to form the lodes. They attain 2100 meters (7000 feet) in length, average 5 meters (9 feet) in width and have been followed downward over 1600 meters (5300 feet).

The ores consist of disseminated galena, sphalerite, pyrite, and argentiferous tetrahedrite. Some pyrrhotite, boulangerite, magnetite, arsenopyrite and some copper minerals occur in minor amounts. The ores carry approximately 6% lead, 3% zinc, and 62.5 grams of silver per metric ton (2 ounces per short ton).

The Sunshine mine produces the most silver and antimony in the U.S. Four others in the district, including the Bunker Hill mine, are third through sixth in lead and zinc production.

The Bunker Hill and associated smelters fill Government Gulch and the adjacent South Fork of the Coeur d'Alene River. The situation is potentially one of the most hazardous in the country. The entire complex drains acidic effluent into heavily inhabited but barren gulches. The smelter stack emissions in Government Gulch have killed nearby vegetation.

Bunker Hill has hundreds of acres of tailing ponds for over four miles in the flood plain of the South Fork of the Coeur d'Alene River, from Kellogg to Pine Creek. The high rainfall of the area provides continual leaching of these huge expanses of tailings. Although now protected by low levees, much of the toxic material has been flooded and leached by excessive runoff from the large cutover drainage basin. Large quantities of various sulfide-processing wastewater are discharged into the river at all flows. It has received mining and raw domestic wastes for over 80 years. In addition to present tailings (contained since 1968), floods release significant quantities of zinc

and other heavy metals from the old stream sediments. The zinc and phosphate plants dump acidic effluent into a heavily inhabited area. Human exposure to cadmium and lead is relatively high (2). Thallium was found in Government Gulch in particulates and mud below the Bunker Hill zinc plant; however, pipe was being laid to divert these wastes into the main tailings pond on the valley flat.

This complex was sampled as far downstream as the level of Coeur d'Alene Lake. Figure 5 is a topographic map of the area showing the locations sampled. The results of this sampling are contained in Table 9.

All outfalls and the larger dumps were sampled. The main Bunker Hill outfall on the river just below Kellogg High School was mostly acid (pH 2.2) and contained definite indications of Tl on preliminary analysis, as did Government Gulch below the acid plant and zinc refinery. A site at the mouth of the South Fork (junction of the main branch and South Fork) of the Coeur d'Alene River yielded an impoverished fauna. However, it was possible to obtain samples of beetles, a mixed sample of mayfly nymphs and cranefly larvae, as well as a sample of algae. The South Fork at Smeltervillie has an average discharge of 641 cubic meters per minute (377 cubic feet per second (cfs)) as measured by the U.S. Geological Survey. Its maximum flood in only 5 years of record was 4998 cubic meters per minute (2940 cfs). The North Fork of the Coeur d'Alene, however, drains relatively unpolluted terrain. Some old mine and placer dredge tailings in Pritchard Creek, 38 km (24 miles) above the junction, extend up to the ghost town of Raven. A relatively clean site was chosen three miles above the junction as control. Separate collections of mayfly nymphs, the stonefly Perlesta, water striders, and cranefly larvae were made. Also, a freshwater sculpin was taken for whole-body analysis.

In samples collected in September 1972, the acidic effluent (Figure 6) at the lead smelter was found to contain 0.02 ppm Tl and the mud washed off the large slag pile (Figure 7) along the south fork of the Coeur d'Alene River was found to contain more than 15 ppm Tl. Mink, Williams, and Wallace (3) found lead, cadmium, zinc, copper, nickel, and iron in the river as a result of sulfide extraction. In addition, thallium has been found in Government Gulch particulates (1.5 ppm) and mud (0.4 ppm) below the Bunker Hill zinc plant. Both of these sources drain into the river, where the mud at the junction of the forks is now found to contain 5 ppm of Tl.

The problem at Kellogg is still far from solved, although diversion of Government Gulch wastes into the tailing pond will help. Until the slag is contained and enough quick lime or alkali is added, toxic metals will continue to enter the Coeur d'Alene River and, thereby, the Spokane water supply (now containing concentrations of Cu and Zn higher than allowed by Public Health Drinking Water Standards).

The data in Table 9 are believed to be a fair illustration of the hazard.

Figure 5. Topographic map of Chinese Mountain and surrounding area.

TABLE 9. CONCENTRATIONS OF HEAVY METALS (ppm) AT SITES NEAR KELLOGG, IDAHO (COEUR D'ALENE RIVER, MAY 1973)

Sampling Location and Type	Thallium	Cadmium	Lead	Copper	Zinc	Indium
Above junction of South Fork (control clean)						
Water	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Mud	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Algae	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Larvae and Nymphs	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Fish	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
South Fork Above Outfalls at High School						
Water	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Mud	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Algae	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Larvae and Nymphs	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Fish	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Tailings Decant Outfall						
Water	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Mud	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Algae	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Larvae and Nymphs	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Fish	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Slag Runoff in 1972						
Water	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Mud	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Algae	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Larvae and Nymphs	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Fish	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Raw Granulating Water						
Water	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Mud	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Algae	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Larvae and Nymphs	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Fish	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Government Gulch at School						
Water	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Mud	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Algae	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Larvae and Nymphs	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Fish	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Fourth Fork at Junction						
Water	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Mud	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Algae	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Larvae and Nymphs	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Fish	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Control larvae are ephemerid. Mud below copper smelter slag was dry. Control algae are probably Spirogyra.

Figure 6. Acidic effluent at zinc refinery in Government Gulch near Kellogg, Idaho.

Figure 7. Slag pile along south fork of Coeur d'Alene River near Kellogg, Idaho.

East Helena, Montana--

The ASARCO zinc smelter on Prickly Pear Creek includes a recently closed lead smelter and Anaconda slag-fuming operation. It is processing 10% sulfur ore from the Texas Gulf Sulfur mine at Timmins, Ontario. Figure 8 shows the location of the ASARCO smelter at East Helena, Montana, and the sites at which samples were collected. The creek is dammed by acres of slag being poured to a height of over 30 meters (100 feet). The hot-water stream running under the slag heap yielded only blue-green algae (Figure 9).

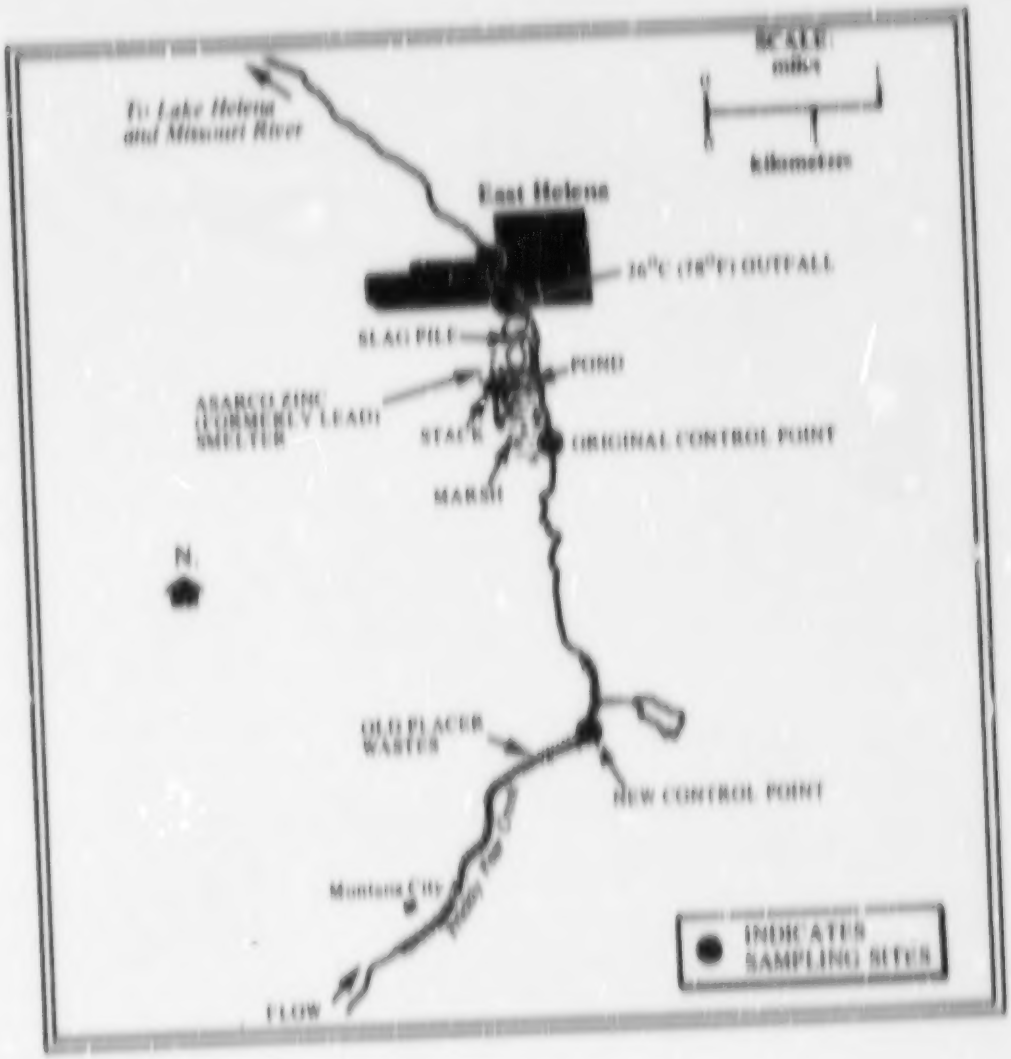


Figure 8. East Helena, Montana, sampling sites.

Figure 9. Hot-water stream running under slag pile (Prickly Pear Creek near East Helena, Montana).

The creek was first sampled in September, 1972, and then on April 30, 1973. The 78°F water which comes from the cooling pond after washing the arsenical speiss (Zn_3As_2), contained plant sewage. No improvements were made in the arrangement of outfalls or wastes between sampling periods.

Just above where the outfall re-entered Prickly Pear Creek, abundant biota were found. The dragonfly nymph Gomphus occurred in small numbers. Caddis larva of the family Hydropsychidae and the stonefly nymphs Perlinella, Isoperla, and Pteronarcella were large and abundant. These were all included in a collection of mixed benthos for analysis. Water striders made a separate sample. A similar collection was made in two locations above the smelter pond. The upstream biota are typical of a clean Rocky Mountain trout stream, even though the stream drains the placer gravels of Montana City. Additional upstream control samples were obtained on Prickly Pear Creek where it runs between old placer gravels in 2-meter (6-foot) high piles and a new paved highway. The new sampling point was located below the new Kaiser cement plant at Indiana, Montana, and above the East Helena smelter. However, fallout from the smelter stacks could have influenced the sample at this point.

An additional downstream sample was taken at the first major irrigation weir below the smelter and town to obtain more invertebrates. Here, the raw sewage from the smelter and town has a more immediate, apparent effect on biological productivity than does heavy-metal pollution.

Data on cadmium and lead found in samples acquired are presented in Table 10. Uncertainties above the detection limit are roughly 10% of the reported value. The septic sediment in mud (oozes) from East Helena showed 8.6 ppm thallium.

Basin, Montana--

A typical small smelter and mill ruins on the Boulder River (Figure 10) were used to process local ore in the last century. Structural collapse allowed collection of flue and grinding dusts from hot locations which are inaccessible in a functioning plant. Slags have been removed and reworked for their metal values. Samples were taken of the large tailing dump along the river, its leachates, and the river water. The river now has a pH of 8.7. Solid wastes contain as much as 5.1% zinc, 1.0% copper, 0.79% lead, 420 ppm cadmium, and 440 ppb thallium. No biota were found. Only 8 ppb of copper was found in the water. Many such small abandoned plants can be found throughout the western mining districts. Containment of their accumulated wastes would be relatively inexpensive in each case if necessary.

TABLE 10. CONCENTRATIONS OF HEAVY METALS (ppm) NEAR EAST HELENA, MONTANA (ASARCO ZINC SMELTER)

Sampling Location	Thallium	Cadmium	Lead
Control*			
Water	–	<0.004	0.1
Mud	–	3.4	50,000
Leaves†	0.083	0.88	22
Roots†	–	10	400
Algae (Spirogyra)	<0.052	1.5-1.8	5.6
Slime**	0.012	–	40
Larvae	–	29-390 (mixed)	70
Water striders	–	4.2	76
Fish (Sculpin)	<0.12	6.3	34
Potential Sources			
78th Smelter Outfall			
Water	–	0.047	0.4
Mud	8.9	1500	190,000
Leaves†	–	–	–
Roots†	1.0	–	–
Algae (Cyanophyta)	0.48	85	1100
Larvae (Caddis)	None	270	1500
Fish	None	None	None
Downstream			
Water	–	<0.002	0.007
Mud	–	170	8000
Leaves†	–	–	–
Roots (Willow)	–	–	1400
Algae	<0.88	200	40-3700
Larvae (Dragonfly)	<0.007	10	330
Water Striders	–	31-74	680
Fish	None	None	None

* Below all placer mining wastes (possibly, also contaminated by backwater and stack dust from smelter).

† Perennial rushes and reeds.

**Diatoms on Spirogyra.

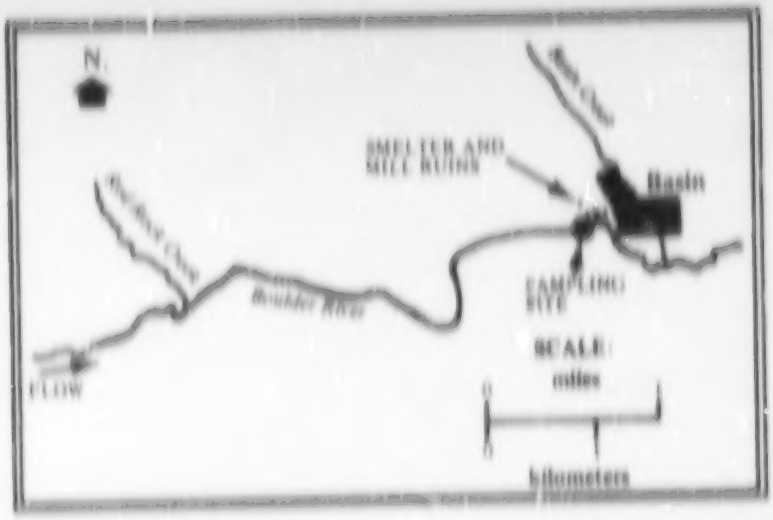


Figure 10. Basin, Montana, sampling site.

Butte/Anaconda, Montana--

Overall description--The copper deposits of the Butte district (Figure 11) are examples of copper mineralization in the form of a great complex of veins. Over 6 million metric tons (7 million short tons) of copper metal have been mined from an area only 4 km (2.5 miles) wide, 8 km (5 miles) long, and about 1.2 km (0.75 mile) deep. In addition, considerable amounts of silver, gold, zinc, and lead, along with some manganese, have been produced.

The host rock is a portion of the granodiorite Boulder batholith near its western border. Porphyry dikes intrude the host rock and are, in turn, cut by seven systems of faults. The ore deposits occur as steeply inclined veins, deposited in these fault systems. They vary in width from 1 to 2 meters (3 to 6 feet) to 10 to 20 meters (30 to 60 feet) and may persist as far as 2100 meters (7000 feet) in length. Each later fault system cuts and offsets the earlier.

The oldest fissures, termed the Anaconda, trend easterly and dip steeply south. They are long and wide, and persist at depth. These veins are rich and rather continuously mineralized, and they have been the great producers at Butte. The Blue system strikes northwest and dips steeply southwest, and its members cut the Anaconda system. Their ore is characteristically discontinous and confined to irregular bodies. A central zone carries copper ores; an intermediate zone contains copper and zinc ores; and an outer zone is dominated by sphalerite along with a little galena, chalcopyrite, and silver; in a gangue of calcite, rhodochrosite, rhodonite, and quartz. These ores yield zinc, manganese,

and silver. They are typical hydrothermal fissure veins in granodiorite of the Boulder batholith. The principal copper minerals are chalcocite, enargite, bornite, chalcopyrite, tennantite, tetrahedrite, and covellite. The gangue minerals are mostly quartz and pyrite. The zinc sulfide, sphalerite, is abundant in certain zones, as is also the manganese carbonate, rhodochrosite.

East of the point where the Anaconda vein becomes discontinuous, mineralization is represented by a series of segments arranged en echelon. Ore in this area occurs in numerous veinlets striking northwest with a stockwork of connecting stringers, irregular lenses, and disseminations of copper-bearing sulfides. This intensely fractured "horsetail" area is about 600 meters (2000 feet) long, 90 to 150 meters (300 to 500 feet) wide, and extends down below the 1020-meter (3400-foot) level.

The vein systems and the "horsetail" zone contain identical ores that apparently were all formed during the same period of mineralization. The later systems are post-mineral faults that cut and displace the ore-bearing veins, giving rise to disconnected segments of the latter.

The Anaconda mill (Figure 1) at the headwaters of Silver Bow Creek processes the large volumes of ore from this pit. The new acid-leaching plant and other modern processing facilities discharge through a series of tanks and ponds into a reservoir in the creek valley with an elaborate floating wastewater facility.

At Butte (Figure 1), the Tl initially found (1972) in the Berkeley Mill effluent (headwaters of Silver Bow Creek), then acid (Table 1), was also found in the crust and mud downstream in the abiotic creek (iron crust-10 ppm/ mud-0.5 ppm; floodplain soil-0.6 ppm). No algae were found. Below Anaconda, pH was restored by the confluence of alkali smelter waster with the acid discharge from the leaching plant in Butte.

Unlike Kellogg, the lower rainfall of Butte and Anaconda makes water rights of value and reuse desirable. Thus, the relative effluent volumes are small. In the first (1972) sampling period, pH values were low. Since that time, however, new water treatment facilities serve to reduce the heavy metal load and, hence, raise pH values.

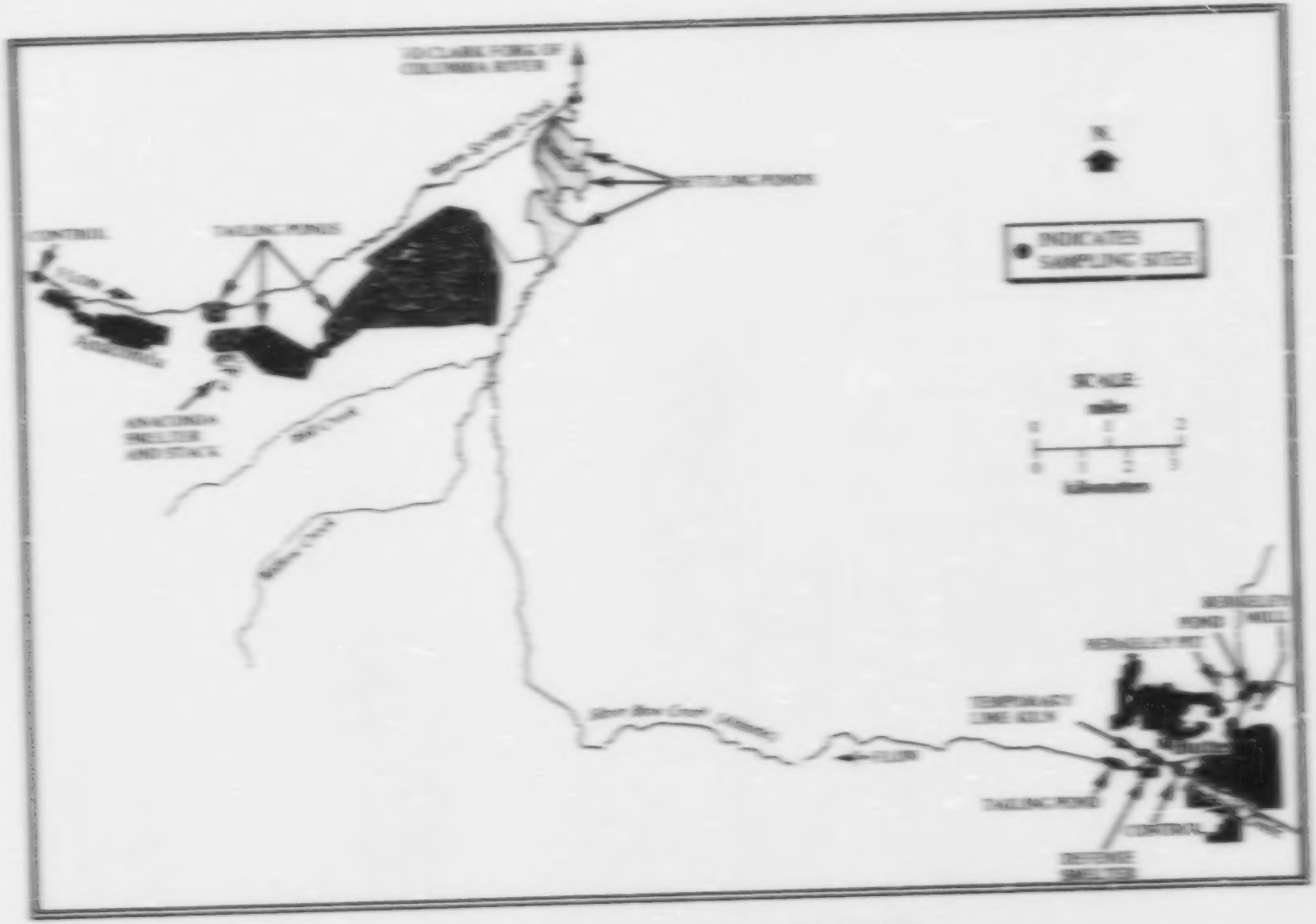


Figure 11. [illegible]

TABLE 11. CONCENTRATIONS OF THALLIUM (ppm) AT SITES NEAR BUTTE/ANACONDA, MONTANA (1972)

Sampling Location	Water	Tailings	Dirt	Flora	Larvae
Control* (Blacktail Creek)	Not Detected			Aquatic Moss <0.01 Aquatic Weeds <0.004	Tipulid <0.073
Potential Sources:					
Berkeley Mill (2 Upstream Sites)	0.2	0.5; 0.81	>10	Lichen	
Downstream in Silver Bow Creek at Defense Smelter	<0.01			Horsetails <0.05	Too Few

*Most upstream tributary to Silver Bow Creek

Defense smelter and Berkeley mill--The abandoned federal smelter on Silver Bow Creek is located just below downtown Butte. In constructing the interstate highway, the creek has been diverted through a new channel blasted in the old slag pile (Figure 12). The pH was so low (4.3) and metals were so concentrated that iron oxides, at least, were precipitating on solid wastes in the channel. Those materials which are being leached or eroded were sampled.

The Defense smelter (Figure 11) had been leased in 1973 by Anaconda and was used as a lime kiln during rebuilding of their kiln at the smelter. The milk of lime produced was being added at the Berkeley Mill, rather than the old procedure of allowing mill and smelter wastes to mix in the settling pond below Silver Bow Creek. Although some additional metal was discharged from the smelter, much less was leaving the mill during sampling in 1973. Table 12 lists the results of the analyses for the samples collected in May 1973. The temporary lime kiln effluent contained 5.5 ppb Tl in waste sediment, carried in the alkaline water.

There was a total absence of benthos all along Silver Bow Creek. However, some aquatic weeds were taken from Blacktail Creek, a tributary draining residential and commercial areas just above the Defense smelter. There are other abandoned plants and waste deposits in the Butte vicinity. All drain into abiotic Silver Bow Creek.

Anaconda smelter--The company smelter complex (Figure 11), the largest single copper source in the U.S., drains into Warm Springs Creek. The tailing ponds extend over 9 km (6 miles) below the smelter to the headwaters of the Clark Fork River (formed by Warm Springs and Silver Bow Creeks), covering at least 10 square km (4 square miles). Calspan sampling covered these wastes and waters.

Figure 12. New stream channel through old slag pile (Silver Bow Creek in Butte, Montana).

TABLE 11. CONCENTRATIONS OF HEAVY METALS (ppm) AT SITES NEAR BUTTE/ANACONDA, MONTANA (MAY 1973)

Sampling Location	Thallium	Cadmium	Lead	Copper	Zinc	Indium
Control: Warm Springs Creek above Anaconda (pH 8.6)						
Water	0.00025	0.003	<0.01	0.022	0.017	<0.1
Mud	<0.02	2.8	22	63	97	0.6
Algae	<0.02	3	28	<7	88	1.1
Larvae and Nymphs	0.053	1.3	0.10	10.15	61.66	0.4
Fish (Sculpin)	0.004	None	None	None	None	1.2
Berkeley Mill (pH 10.3*) (3 Sites)						
Water	<0.0001	0.002	<0.01	0.030	0.023	0.1
Mud	<0.04*	19.5	111	3200	2000	0.9
Algae	None	Nor.1	None	None	None	None
Larvae and Nymphs	None	None	None	None	None	None
Fish (Sculpin)	None	None	None	None	None	None
Defense Lime Kiln (pH 11.5)						
Water	0.00005	0.003	0.03	0.057	0.088	0.25
Mud	◄		Muddy Water			►
Algae	None	None	None	None	None	None
Larvae and Nymphs	None	None	None	None	None	None
Fish (Sculpin)	None	None	None	None	None	None
Anaconda Smelter (pH 8.4)						
Water	<0.0001	0.001	0.02	0.06	0.11	<0.1
Mud	0.04	2.8	91	1100	1360	0.4
Algae	None	None	None	None	None	None
Larvae and Nymphs	None	None	None	None	None	None
Fish (Sculpin)	None	None	None	None	None	None
Clark Fork below Warm Springs Creek						
Water	0.00018	0.004	<0.01	0.048	0.21	<0.1
Mud	<0.03	3	25	480	900	0.3
Algae	None	None	None	None	None	None
Larvae and Nymphs	<0.07	<0.7	34	78	320	<0.7
Fish (Sculpin)	None	None	None	None	None	None

*10 in 1972

The Anaconda smelter is the only industry in the valley since a zinc smelter was closed in 1969. The large copper smelter reduced polymetallic-sulfide concentrates from the mill in Butte. The biota within five miles of the smelter was severly limited by heavy-metal and sulfur toxicity. Very old, hardy shrubs, Tetradymia and Chrysothamnus, and a few cottonwoods and willows barely survive. Reedgrass (Calamagrostis montanensis) exists temporarily on clean, newly eroded soil. No wild animals or mature insects can be found (Mumshower, J., personal communication, 1972). The wastewater handling facilities resemble those at the mill in Butte. Arsenic exposures are relatively high in Anaconda (2).

The Clark Fork site sampled receives acid wastes from the Butte mill which are partially neutralized by alkaline (pH 12.7) smelter effluent from the settling ponds (subject to winter overflow). This portion of the river is also contaminated by partially treated sewage from the town and nearby state hospital.

An uncontaminated site on Warm Springs Creek above the town of Anaconda was sampled for control. A large species of the caddis larva family Hydropsychidae formed one collection. A giant stonefly nymph, Pteronarcella, formed another collection. Several caddis larvae Brachycentrus were removed from their cases and stored for analysis. In the following spring collection, stoneflies included Arcynopteryx, Pteronarcella, and Perlinella; mayflies included Ephemerella, Arthroplea and Potamanthus; caddisflies were Hydropsychiad and Psychomylid.

Warm Springs Creek upstream from Anaconda contains 0.25 ppb Ti in the water. Although the drainage basin is now almost uninhabited grazing land, it contains old mine workings, dumps and many prospect pits in a locally complex volcanic terrain recently heavily glaciated.

Ti may be leaching out of both the old mining debris and glacial till. The large mayfly larvae contain 3 ppb Ti and a small sculpin contains 4 ppb Ti, showing a bioconcentration factor of 12-16 times the concentration in water. Smaller, rarer mayfly larvae collected at this site in the fall contained 200-240 ppb Ti. They have accumulated through the open-water season a bioconcentration factor of almost 1000. This contamination was reduced to less than 0.1 ppb above Anaconda as side gulches diluted it. The mine-debris and glacial-till leach cannot be the source of all the Ti still found in Clark Fork. At least 40 ppb Ti in mud was entering from the smelter due to low pH (Table 12). The other control stream, Blacktail Creek at Butte (Table 11), showed no Ti.

For comparison, the Ti concentrations sampled in September 1972 from the Berkeley Mill at Butte were up to 0.8 ppm in the mill effluent water (pH 2.6), about 0.55 ppm in the mud (tailings), and over 10 ppm in the iron crust deposited in the stream bed. It is clear that the acid discharge from the mill carried more toxic heavy metals.

As an additional check, Silver Bow Creek was sampled between the mill outfall and the junction of Blacktail Creek at George and Kaw Streets. The analysis closely confirms the data from the mill outfall for all metals in both water and mud.

Selby, California--

A few reconnaissance samples were taken on 27 August 1973 from the abandoned ASARCO non-ferrous smelter[5] at Selby, California (Figure 13). This site, which has been used for nearly a century, has a large pile of slag poured into the bay. Sediment, algae, water, and a representative small fish were collected on the beach eroded into the slag pile. In addition, bay water from across the Carquinez Strait and Pacific Ocean water from off Monterey were sampled for comparison.

Lead at a concentration of 3 ppm, along with 240 ppb copper and 450 ppb zinc, were found in a stagnant pond draining the slag pile.

The pond and its outfall (diluted by the bay tide) showed no excess cadmium over controls (50-100 ppb) from elsewhere in the bay. Green algae (Ulva) near the outfall contained 5.3 ppm lead (as compared with 3.6 ppm across the straits at Nesre Island) and 0.18% zinc (as compared with 4.7 ppm). Cadmium and copper were not significantly concentrated, nor were the other samples. Thallium was not detected except in soil near the stack (320 ppb).

Southwestern U.S.

Synopsis--

Copper mining, milling and smelter operations in the Southwest were sampled from the Colorado River to the Rio Grande. In this arid region, water is expensive. Most facilities store and recycle all of the water, including rainfall, which falls on the mine, tailings, or slag and runoff. Results of sampling in January, 1973 from the copper processing plants in this area are discussed below.

Porphyry District--

Overall description--The Arizona/New Mexico/West Texas porphyry copper mining district, which supplied most of the Cu today, is in a very dry climate with few permanent streams. The centrally located smelters and acid plants at Hayden, however, are directly on the Gila River, which is one of the principal sources of irrigation water for Arizona agriculture.

[5] It is historically interesting that Cottrell's first precipitator was operated in the acid plant at this facility.

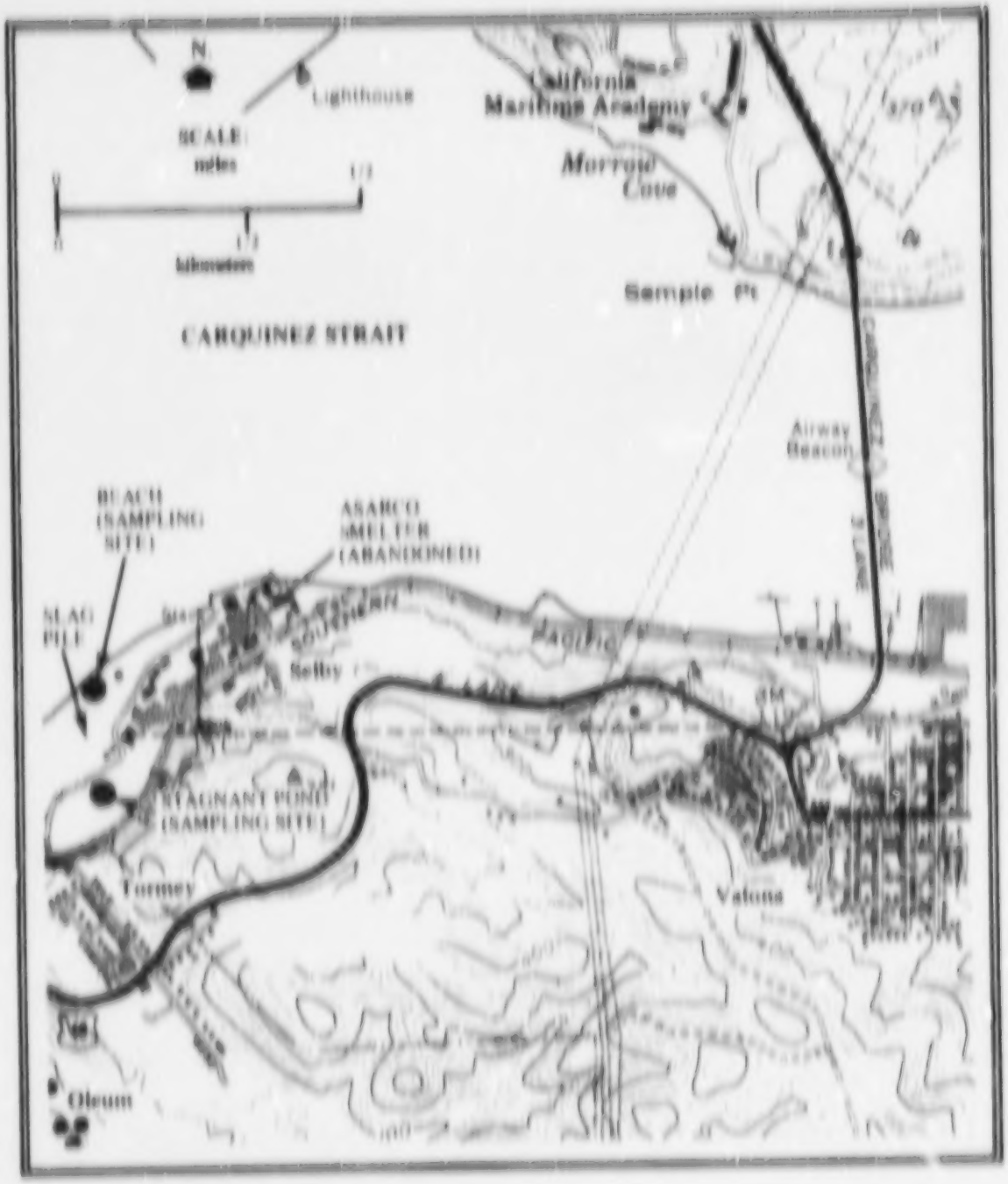


Figure 13. Selby, California, sampling sites.

The Ajo, Douglas, Duval, and other mines in the porphyry belt south of Tucson have no surface runoff to ocean or irrigation.

The porphyry district is underlain by the late-pre-Cambrian sediments found in Montana and Idaho. This thick series includes the Pinal schist, a metamorphosed cupriferous blackshale which can be correlated with the ore at White Pine, Michigan. The copper was mobilized by hot igneous intrusions and crystallized in the partially quenched (200°-300°C) (392°-572°F) rim of large ivory-colored oligoclase feldspar ($NaAlSi_3O_8$ with 10 to 30% $CaAl_2Si_2O_8$) crystals in a purple ground-mass of fine-grained minerals. The overlying Paleozoic limestone trapped the richest ore bodies (skarns) where they were cut by porphyry stocks, particularly immediately below shales.

Phelps-Dodge operations at both Morenci, Arizona, and Tyrone, New Mexico, are so combined that water is fully recycled. Location of facilities is partially controlled by access to water.

Kennecott, at both Hayden/Ray, Arizona, and Chino/Hurley, New Mexico, still uses a mill at the smelter rather than close to the mine.

Hayden/Ray, Arizona--Sampling locations in the Hayden/Ray vicinity, Arizona, are shown in Figure 14.

The Kennecott Ray pit, almost 3.2 km (2 miles) across, is in a large blanket ore deposit in the Pinal schist drained by Mineral Creek (sampled below the acid leach plant and at Kelvin where it joins the Gila River).[a] Only the Kennecott pit at Ray, Arizona, has a large runoff problem, which will eventually be corrected by a long diversion tunnel. All of the facilities whose runoff could enter surface irrigation or domestic supplies were sampled. The creek ran copper-blue. It was abiotic below the mine, as was the Gila River below its confluence. There was no recycling, and this stream provided most of the water for citrus and lettuce irrigation below Florence at low flow. Biota were collected above Mineral Creek and above the mill/smelter outfall at Hayden. The Kennecott Hayden mill/ smelter complex recycle system was incomplete. Runoff water precipitated metal deposits in Hayden (sampled). It drained from a tailing pond, second in size only to Anaconda. The ASARCO smelter and acid plant recycle all water but cause heavy fumes down the Gila Valley. Results of thallium, cadmium, and lead analyses for water, sediments algae, and biota are given in Table 13.

Mammoth, Arizona--The large, low-grade San Manuel (Tiger) stock of Magma Copper Co. is mined on the pediment draining into the usually dry San Pedro River (sampled) which joins the Gila at Hayden (Winkelman). The new Mammoth mill/smelter complex impounds tailings behind cyclone-separator dams, as in Missouri. Water is recycled. Results of analyses for thallium, lead, and cadmium are given in Table 14.

[a]Figure 15 shows a photo of Mineral Creek at the acid leach plant where samples were taken.

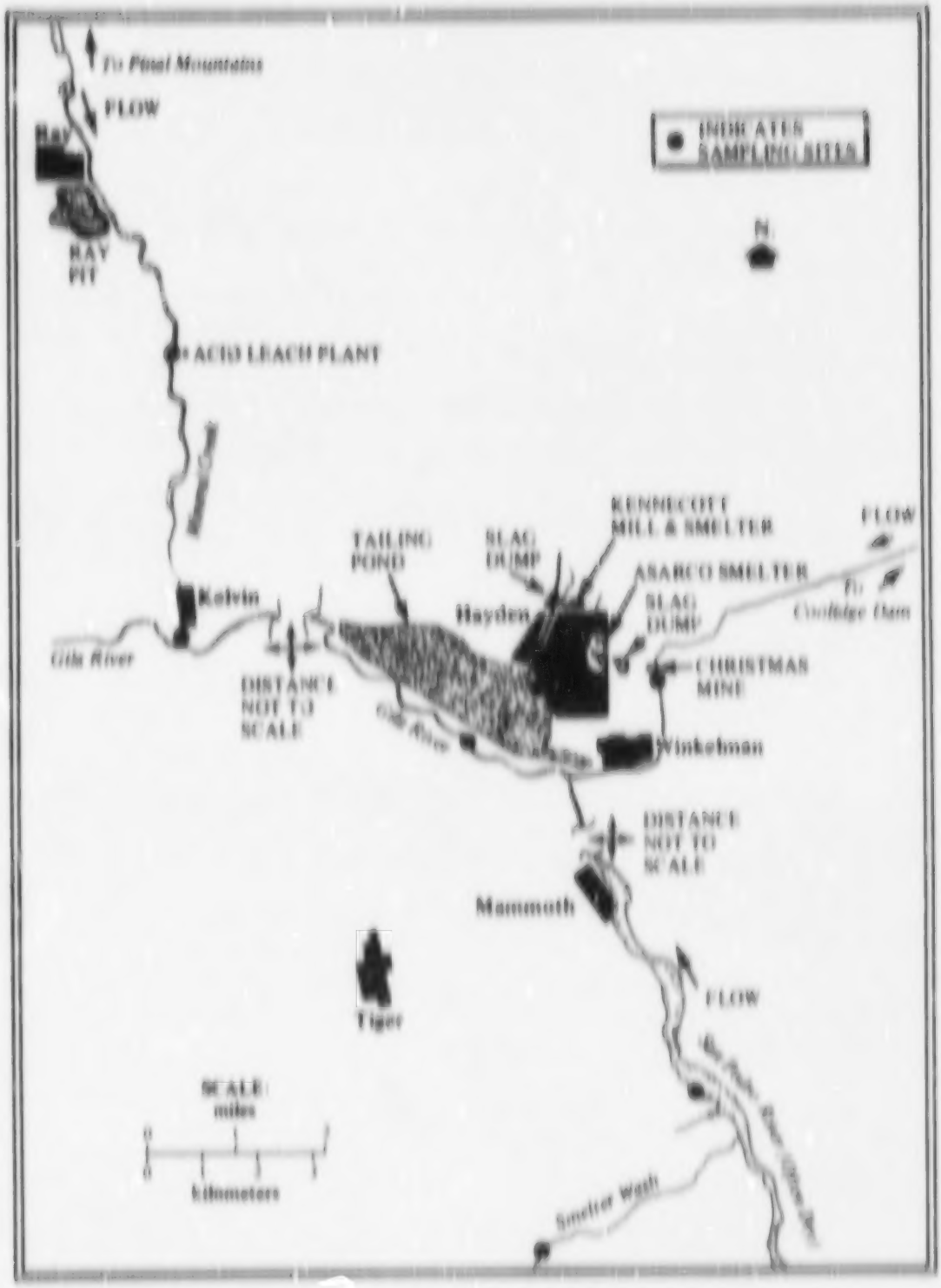


Figure 14. Hayden/Ray/Mammoth, Arizona, sampling sites.

TABLE 15. CONCENTRATIONS OF HEAVY METALS (ppm) NEAR HAYDEN/RAY, ARIZONA AREA (KENNECOTT COPPER CO. AND ASARCO)

Sampling Location	Thallium	Cadmium	Lead
Gila River above Hayden (below Christmas Mine)			
Water	<0.003	<0.0005	<0.005
Sediment	0.27	0.53	65
Algae	0.56	0.76	1,251,000
Larvae (Caddis and Blackfly)	–	–	600
Fish	–	0	–
Kennecott Smelter			
Water	<0.003	0.002	0.01
Sediment	0.12	1.1	2140
Algae	◄	Nothing alive	►
Larvae	◄	Nothing alive	►
Fish	◄	Nothing alive	►
ASARCO Smelter			
Water	<0.003	0.0005	<0.01
Sediment	0.16	0.6 1.3	23,200
Algae	◄	Nothing alive	►
Larvae	◄	Nothing alive	►
Fish	◄	Nothing alive	►
Ray Pit			
Water	◄	Drains into Mineral Creek	►
Sediment	0.11 0.15	2.4	8200 9400
Algae	◄	Nothing alive	►
Larvae	◄	Nothing alive	►
Fish	◄	Nothing alive	►
Mineral Creek			
Water	0.004 0.005	0.048	0.01
Sediment	0.12	0.3 0.35	1340 1320
Algae	◄	Nothing alive	►
Larvae	◄	Nothing alive	►
Fish	◄	Nothing alive	►
Gila River below junction with San Pedro River			
Water	0.003	0.017	0.015
Sediment	0.11	0.49	1180
Algae	◄	Nothing alive	►
Larvae	◄	Nothing alive	►
Fish	◄	Nothing alive	►

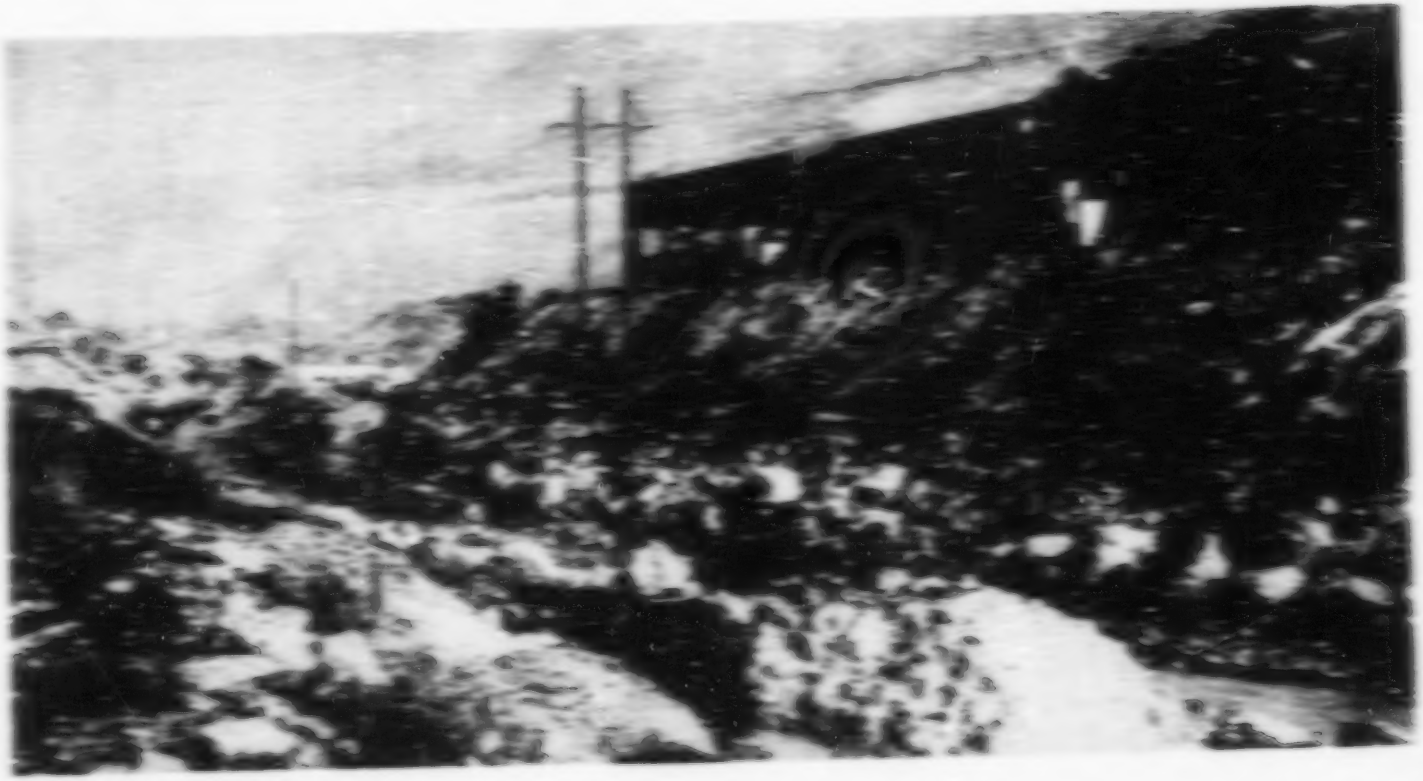


Figure 15. Mineral Creek at the acid leach plant near Kelvin, Arizona.

TABLE 14. CONCENTRATIONS OF HEAVY METALS (p.p.m) NEAR MAMMOTH, ARIZONA (MAGMA COPPER CO.)

Sampling Location	Thallium	Cadmium	Lead
Mammoth Mill			
Water	–	recycled	recycled
Sediment	–	0.43	2170
Slime	◄	Nothing alive	►
Algae	◄	Nothing alive	►
Larvae	◄	Nothing alive	►
Mammoth Smelter			
Water	–	recycled	recycled
Sediment	–	0.24	3850
Slime	◄	Nothing alive	►
Algae	◄	Nothing alive	►
Larvae	◄	Nothing alive	►
San Pedro River below mill and smelter			
Water	<0.003	<0.0006	<0.01
Sediment	<0.12	0.5	60
Slime	0.016	–	7.5
Algae	–	–	20
Larvae (Blackfly)	–	>0.8	>160

Globe/Miami/Superior, Arizona--The layout of the Globe/Miami/Superior area is shown in Figure 16. The middle of the mountain range is occupied by barren, coarse Schultze granite. On the east side, the 4-km (2.5-mile)-long Miami-Inspiration lode forms a rim around a lobe of porphyry. The Inspiration smelter sits on a 75-meter (250-foot)-high pinnacle of ore surrounded by windblown tailings and slag (sampled). The water from the smelter and mill is recycled through the acid leach (sampled). The Inspiration mill, the Ranchers Exploration and Development Corp. Bluebird mine/mill (sampled) in Bloody Tanks Wash (control samples above Bloody Tanks), the ruined smelter in Globe (slag sampled), and the CITGO (Cities Service) and AMAX (American Metals Climax molybdenum) operations up Pinhorn Wash drain into dry Pinal Creek, a tributary of the Salt River, which was sampled below Radium. Analyses of water, sediments, and biota are given in Table 15.

On the west side of the Pinal Mountains, the Magma Copper Co. at Superior (discussed later) permanently transferred smelting operations to Mammoth (discussed below) during a strike in 1970. In the original Magma mine, still operating up the mountain above the mill and closed smelter, the mineral relations of porphyry copper have been worked out in greatest detail. The hot cupriferous water flowed along shear zones to deposit massive sulfides in the thin coralline Martin limestone (Devonian Onondaga equivalent). Analyses of water, sediment, and cattails from this old mining area are given in Table 16.

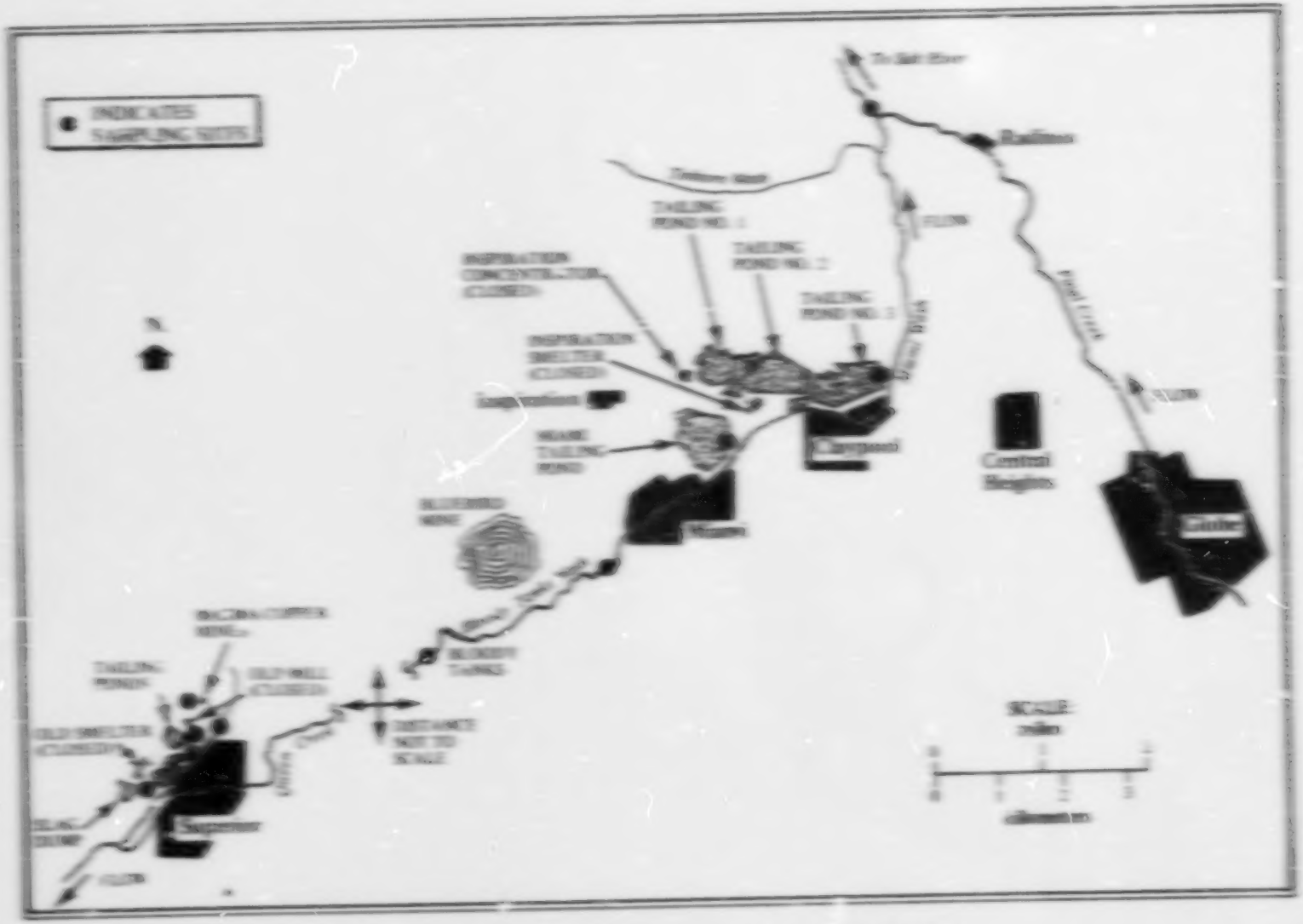


Figure 16. Globe/Miami and Superior, Arizona, sampling site.

TABLE 15. CONCENTRATIONS OF HEAVY METALS (ppm) NEAR GLOBE/MIAMI, ARIZONA (INSPIRATION CONSOLIDATED AND AMAX)

Sampling Location	Cadmium	Lead
Control:		
Bloody Tanks Wash Upstream of Mine		
Water	--	<0.005
Sediment	--	114
Phreatophyte Roots	--	28
Bluebird Mine Runoff into Wash		
Water	0.0018	0.018
Sediment	<0.05	386
Phreatophyte Roots	None	None
Inspiration Concentrator (part of Mill)		
Water	78 recycled	190 recycled
Sediment	2.5	42,000
Phreatophyte Roots	0.69	18
Inspiration Smelter (part of Mill)		
Water	78 recycled	190 recycled
Sediment	1.5	0.150
Phreatophyte Roots	0.9	380
Pinal Creek below Miami Wash		
Water	Flood only	Flood only
Sediment	<0.05	310
Phreatophyte Roots	None	None

TABLE 16. CONCENTRATIONS OF HEAVY METALS (ppm) NEAR SUPERIOR, ARIZONA (MAGMA COPPER COMPANY)

Sampling Location	Thallium	Cadmium	Lead
Queen Creek Draining Magma Mine			
Water	0.0021	<0.0005	<0.01
Sediment	0.11	2.6	18,600
Cattails	--	None	None
Ore from Mine			
Water	--	None	None
Sediment	--	1.9	28,400
Cattails	--	None	None
Old Mill (closed)			
Water	0.0031	0.0005	<0.01
Sediment	0.089	1.8	1,900
Cattails	--	0.05	16.7
Old Smelter (closed)			
Water	--	0.0045	<0.01
Sediment	--	0.82	1870
Cattails	--	None	None

Morenci, Arizona--The Phelps-Dodge large open-pit mine and mill/smelter complex, shown in Figure 17, recycles water from Chase Creek. The creek is dry below the complex. This creek drains into the San Francisco River, which drains into the Gila below Clifton. A new company town has been built on the old tailings. Water from the river, wastes, and mud from these operations and a ruined smelter site on the river were sampled. Results of these analyses are given in Table 17.

TABLE 17. CONCENTRATIONS OF HEAVY METALS (ppm) NEAR MORENCI, ARIZONA (PHELPS DODGE CO.)

Sampling Location	Thallium	Cadmium	Lead
Control:			
San Francisco River above Clifton			
Sediment	--	--	60
Phelps Dodge Morenci Open Pit Mine			
Sediment	--	4.0	2000
Larvae	--	None	None
Phelps Dodge Smelter			
Sediment	--	4.0	13,000
Larvae	--	None	None
Phelps Dodge Smelter			
Sediment	--	0.60	1000-5000
Larvae	--	None	None
Chase Creek above Clifton			
Sediment	--	1.0	1000
Larvae	--	None	None
Clifton (Arizona Copper Co.) Smelter (Ruined)			
Firebrick			
Sediment	0.10	270	100,000
Larvae	--	None	None
Slag			
Sediment	--	<0.60	1000
Larvae	--	None	None
San Francisco River (downstream at Ward Canyon Road)			
Sediment	0.60	<0.60	70
Larvae (Caddis and Blackfly)	--	2.5	60

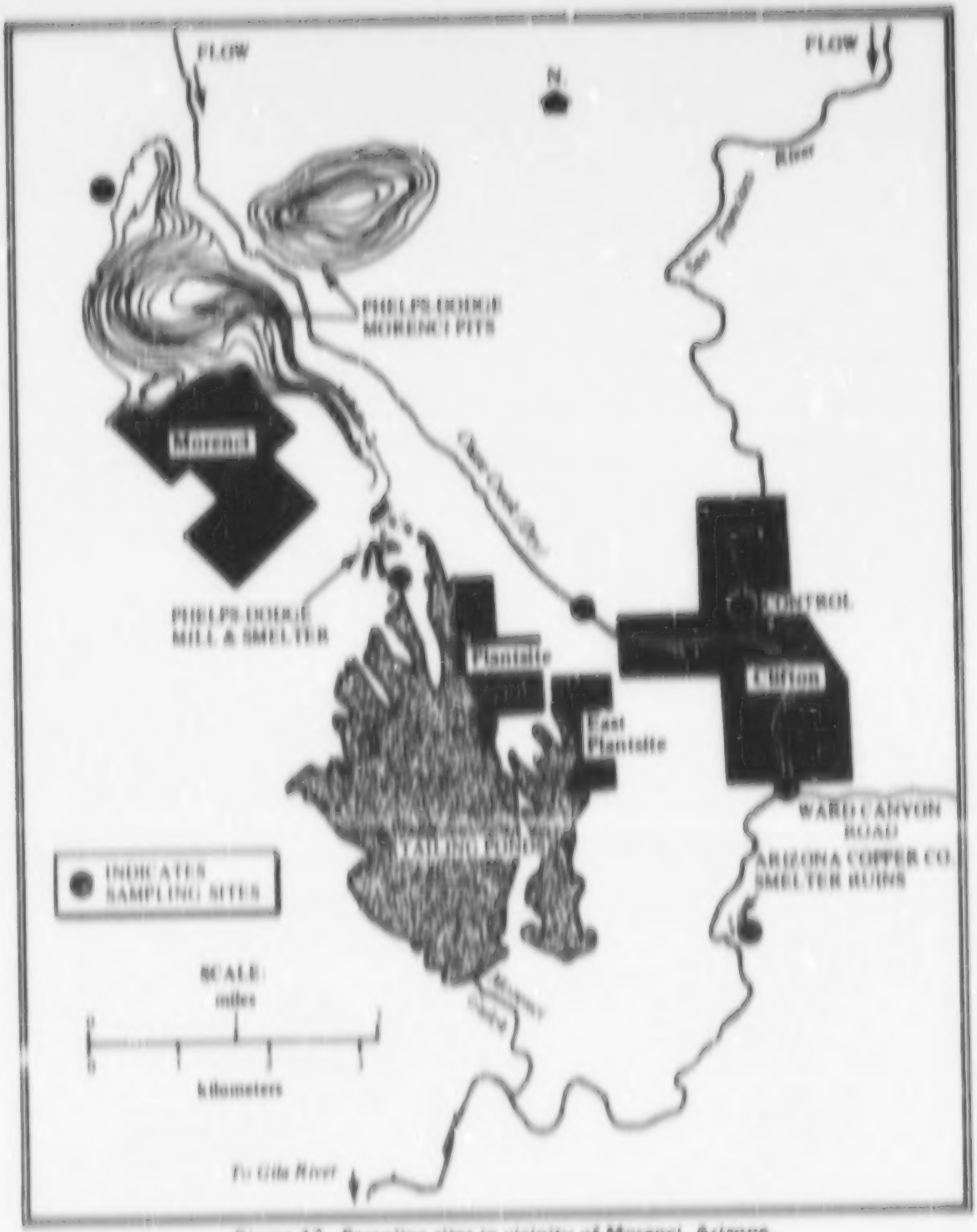


Figure 17. Sampling sites in vicinity of Morenci, Arizona.

Pierro, Chino/Hurley, and Tyrone, New Mexico--The east end of the porphyry district shown in Figure 18 produces significant zinc as well as copper and molybdenum. The Phelps-Dodge pit and mill at Tyrone in the Big Burro Mountains, drains through dry washes (sampled, along with waste) into the Mimbres River. Water from the tailings is recycled.

In the Cobre Mountains, copper occurs around Laramide (50 million years old) porphyritic quartz monzonite stocks in a north/south trend which is followed by Whitewater and associated creeks below the U.V. Industries mine and mill at Pierro. The recycled U.V. Industries water and sediment was sampled, as was the tailing runoff water and sediment at the headwaters of Whitewater Creek. Hanover Creek, which joins Whitewater Creek at Hanover Junction, flows past a closed mill (where biota were sampled), through Hanover, and near Turnerville (mine waste and runoff sampled). The ASARCO Groundhog mine was also sampled (no biota present).

The 1.6-km (1-mile)-wide Kennecott Chino pit (Figure 19) on a stock east of the trend has removed everything east of Turnerville, including the site of the former town of Santa Rita. 75% of the rock was hauled to waste piles above the pit and leached with acid (Figure 20) (sampled in the tributary creek below and above at the acid-leach and recycling points). The rest was hauled to the mill and smelter downstream at Hurley (slag, soil, tailings, and effluent sampled). Analyses of water, sediments, and biota from this region are given in Table 18.

Below the huge Kennecott mountain of tailings, Whitewater Creek disappears into the desert, although the peak flood waters reach the Mimbres River and the irrigated cotton fields at Deming. Acid fumes from the Kennecott acid plant and smelter at Hurley created serious vegetation damage as far up as Hanover.

El Paso, Texas--The ASARCO smelter is still operating on the Rio Grande (Figure 21). All river water used is recycled and evaporated. The smelter originally processed ores from the entire porphyry district as well as from Chihauhua and Sonora, Mexico. At present, old slag (sampled) is being crushed and sold. Soil samples, mud samples from the dry wash carrying smelter runoff, and river samples (water, muds, and biota) were collected above and below the plant. Results of analyses are given in Table 19. The data indicate that toxic lead, thallium, and cadmium fumes released from smelter stacks settle in soils and sediments but are not solubilized in water to any great extent.

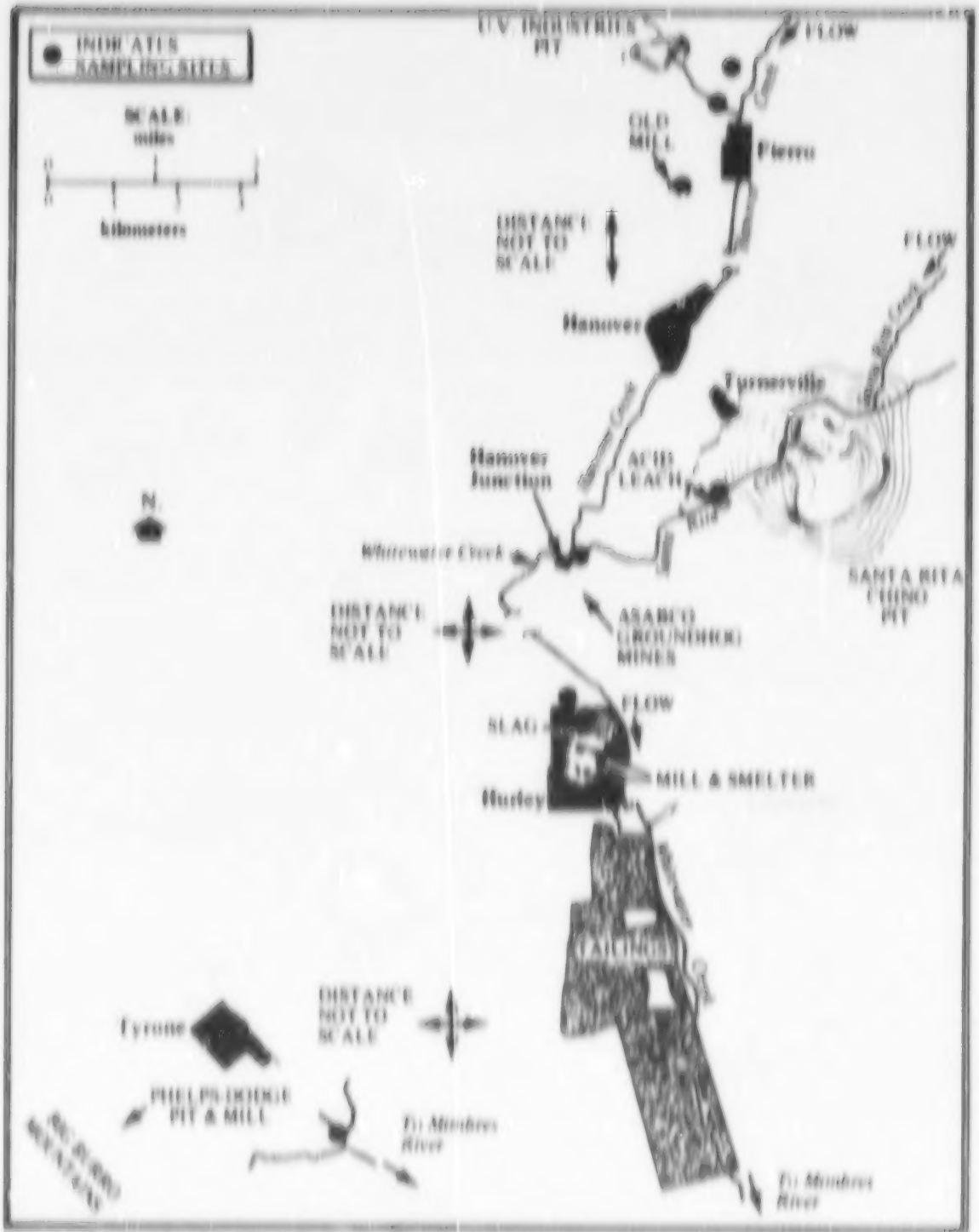


Figure 18. Sampling sites near Fierro, Chino/Hurley, and Tyrone, New Mexico.

Figure 19. Santa Rita Chino pit.

Figure 20. Waste pile and acid leach runoff above Santa Rita Chino pit.

TABLE 18. CONCENTRATIONS OF HEAVY METALS (ppm) NEAR FIERRO, CHINO/HURLEY, AND TYRONE, NEW MEXICO

Sampling Location	Thallium	Cadmium	Lead
U. V. Industries, Inc., Pit at Fierro			
Water (Recycled)	<0.003	0.0021	0.02
Sediment	<0.08	7.8	1540
Larvae (Midge)	--	None	None
Old Mill Near Fierro			
Water	<0.003	0.0008	<0.01
Sediment	0.51	16.08	1100-3140
Larvae (Midge)	--	0.8	536
Kennecott Copper Co.			
Santa Rita Pit			
Water	◄	To leach	►
Sediment	<0.08	0.8	99,000
Larvae	◄	Nothing alive	►
Acid Leach			
Water (Recycled)	0.008	0.18	0.03
Sediment	1.88	4.3	3500
Larvae	◄	Nothing alive	►
To Irrigation at Hanover Junction			
Water	0.0037	0.18	0.09
Sediment	<0.14	0.6	448
Larvae	◄	Nothing alive	►
Hurley			
Below Mill			
Water	<0.003	0.0008	0.01
Sediment	0.082	0.17	218
Larvae	◄	Nothing alive	►
Below Smelter			
Water	◄	Recycled	►
Sediment	0.19	1	2180
Larvae	◄	Nothing alive	►

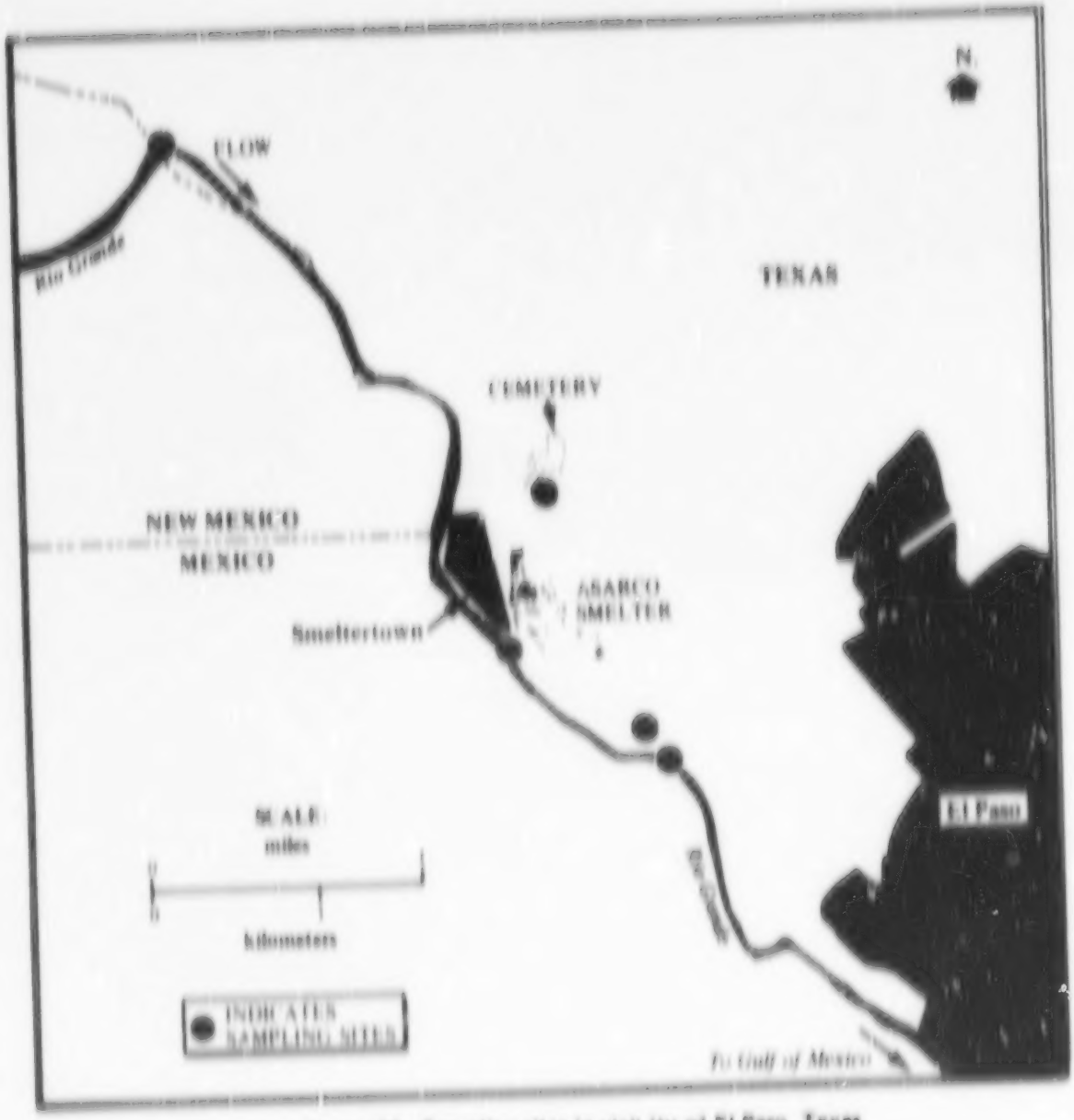


Figure 21. Sampling sites in vicinity of El Paso, Texas.

TABLE 19. CONCENTRATIONS OF HEAVY METALS (ppm) NEAR EL PASO, TEXAS (ASARCO SMELTER)

Sampling Location	Thallium	Cadmium	Lead
Rio Grande			
Upstream			
Water		0.0008	0.03
Sediment		3	410
Algae		4.4	765
Smelter			
Water		Recycled	Recycled
Sediment		7.1	16,200
Algae		None	None
Wash Draining Smelter			
Water		Flood only	Flood only
Sediment	0.5	19	11,000
Algae		None	None
Cemetery Soil Under Stack			
Water		None	None
Sediment	0.5	7.5	5140
Algae		None	None
Downstream			
Water		--	--
Sediment		13	1370
Algae		3	48

Summary of porphyry district findings--In summary, the porphyry copper belt wastes had high measured lead concentrations, probably as a result of no present lead recovery from these ores. The largest source of pollution as previously reported was Mineral Creek (Table 17, Figure 14) draining the Kennecott-Ray pit into the Gila River. The next largest operations were at the Kennecott-Santa Rita Pit on Whitewater Creek (Table 18, Figure 18). Although most of the flood flow of Whitewater Creek was used to irrigate cotton around Deming, New Mexico, some alfalfa was grown and fed to beef cattle. The low flow went to ground water recharge, where ion exchange capacity was sufficient to remove most toxic metals. Some of the mine wastes found at Santa Rita had as high as 3.5% lead (but is essentially cadmium-free). It was eroding and leaching rapidly.

Magma Copper Co. operations at Mammoth (Table 14) and Superior (Table 16, Figure 16) are well dammed off from permanent surface streams although these, like all tailing dams, are subject to rainwash. Thalliferous slime in the San Pedro River was probably related to sewage treatment of domestic wastes from the town site.

The only thallium found in Globe/Miami (Table 15, Figure 16) was 5 ppb in the acid leach water which was recycled through the mine wastes. No cadmium was found at the control site upstream (less than 0.5 ppb in water and 50 ppb in sediment and biota). At Globe, the ruined Miami Copper Company (now Cities Service) smelter site had over 20 hectares (50 acres) of old slag containing 98 ppb of thallium which was eroding into Pinal Creek.

No toxic metals were observed in the Phelps-Dodge operations or on the San Francisco River below Clifton, Arizona (Table 17, Figure 17), although flood erosion and leaching were a potential hazard. At Tyrone, New Mexico, a sample of exposed mine wastes contained 75 ppb thallium, 43 ppm cadmium, and 0.52% lead.

Planet Mine (Parker), Arizona--

The Planet Mine, now closed, was sampled in January 1973. It produced the representative, high-temperature ores that are close to the active rhyolite volcanism and copper mineralization of the Salton Sea. The mine is on the Bill Williams River, which drains into the Colorado above Parker, Arizona (across from Earp, California) (see Figure 22). During operations from 1966 to 1970, a coarse, poorly controlled acid leach was used to extract copper from the hematite-magnetite (Fe_2O_3-Fe_3O_4) ore sampled. Wastes sampled could be carried down the dry Planet Wash to the river during floods (Figure 23).

The highest concentration of thallium found in the Southwest--5 ppm--was found at the closed Planet Mine (Table 20). The Colorado River below the Bill Williams River and Planet Mine had the highest regional background, with 21 ppb of thallium. It is an area of natural metal concentration.

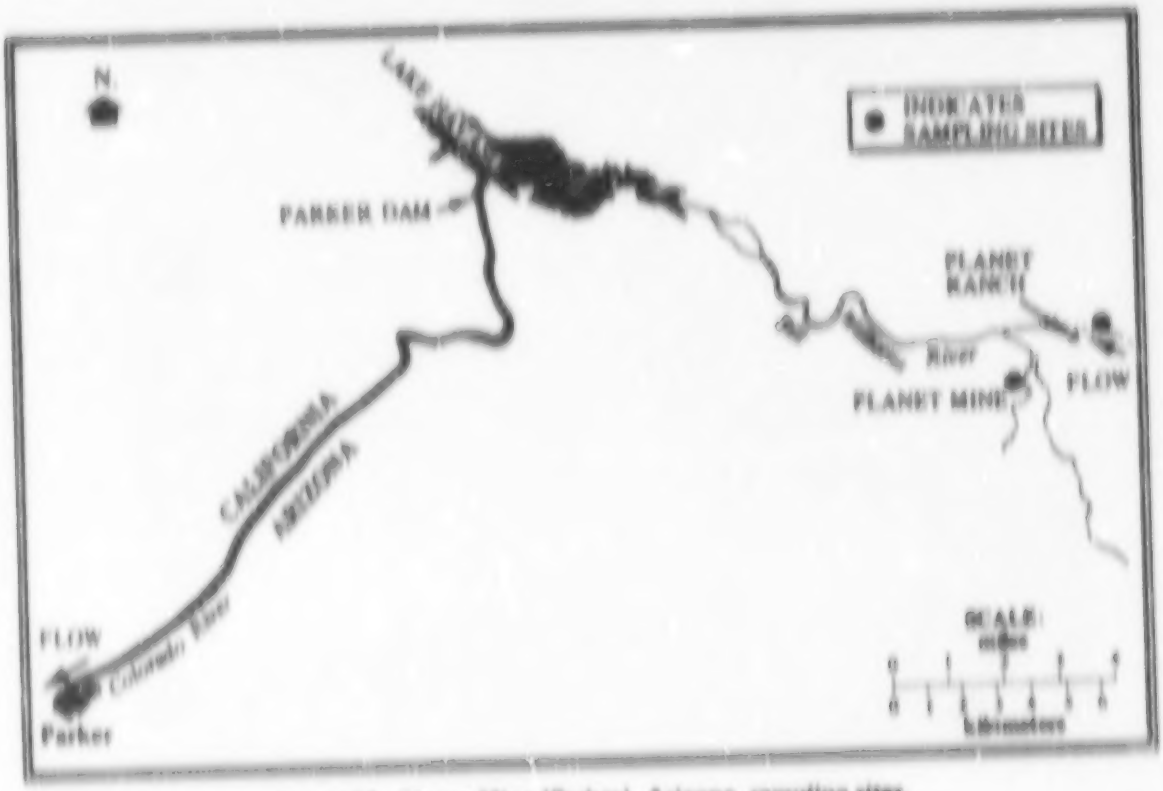


Figure 22. Planet Mine (Parker), Arizona, sampling sites.

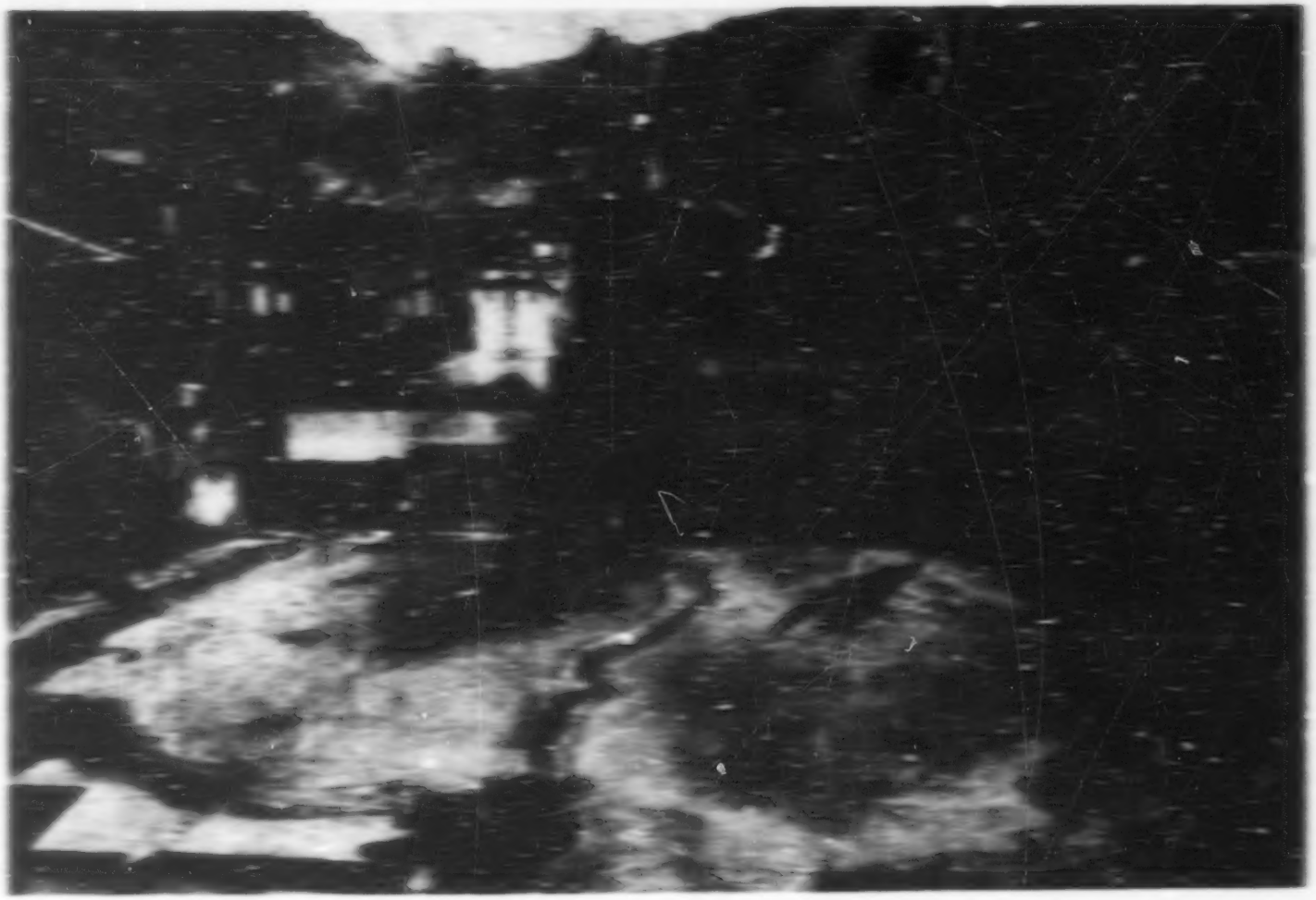


Figure 13. Planet Mine and dock.

TABLE 20. CONCENTRATIONS OF HEAVY METALS (ppm) NEAR PLANET MINE, PARKER, ARIZONA (POWDERED METALS CORP., JANUARY 1973)

Sampling Location	Thallium	Cadmium	Lead
Planet Mine Acid Leach (Closed)			
Water	--	--	Dry
Sediment	0.1	195	34,000
Algae	None	--	None
Grass Roots	--	None	None
Larvae (Blackfly)	--	None	None
Clams	--	None	None
Fish	--	--	None
Bill Williams River at Planet Ranch below Mine Wash			
Water	--	--	0.01
Sediment	<0.11	1	97
Algae	0.031	--	18
Grass Roots	--	0.23	30
Larvae (Blackfly)	--	0.4	42
Clams	--	None	None
Fish	--	--	0.001
Colorado River at Parker below Bill Williams River			
Water	--	--	<0.01
Sediment	0.021	0.06	37
Algae	<0.07	--	110
Grass Roots	--	--	--
Larvae (Blackfly)	--	None	None
Clams	--	13	170
Fish	--	--	--

Midwestern U.S.

Mid-continent Lead/Zinc Region--

Thallium is not significant in the extensive low-temperature lead/zinc ores of the mid-continent: Wisconsin, Illinois, Missouri, Kansas, Oklahoma, and Arkansas. Only those smelters in the midwest which have used or are using significant amounts of Cordilleran or foreign ores and which meet the established criteria (Section 5) were included in the study locations. With the exception of the single refinery located in East St. Louis, Illinois, all of these smelters are located in southeastern Missouri surrounding the so-called New and Old Lead Belts of that state. The limits of the Missouri study area, the approximate limits of the Missouri Lead Belts, and East St. Louis are shown in the locator map of Figure 24. The Missouri study area is depicted in detail in Figure 25.

Missouri New Lead Belt (Viburnum Trend)--

Overall description--A field sampling program was conducted in the Missouri New Lead Belt, or Viburnum trend, and associated processing facilities.

Figure 2A. Missouri New and Old Lead Belts in relation to area of Missouri sampled (shaded area).

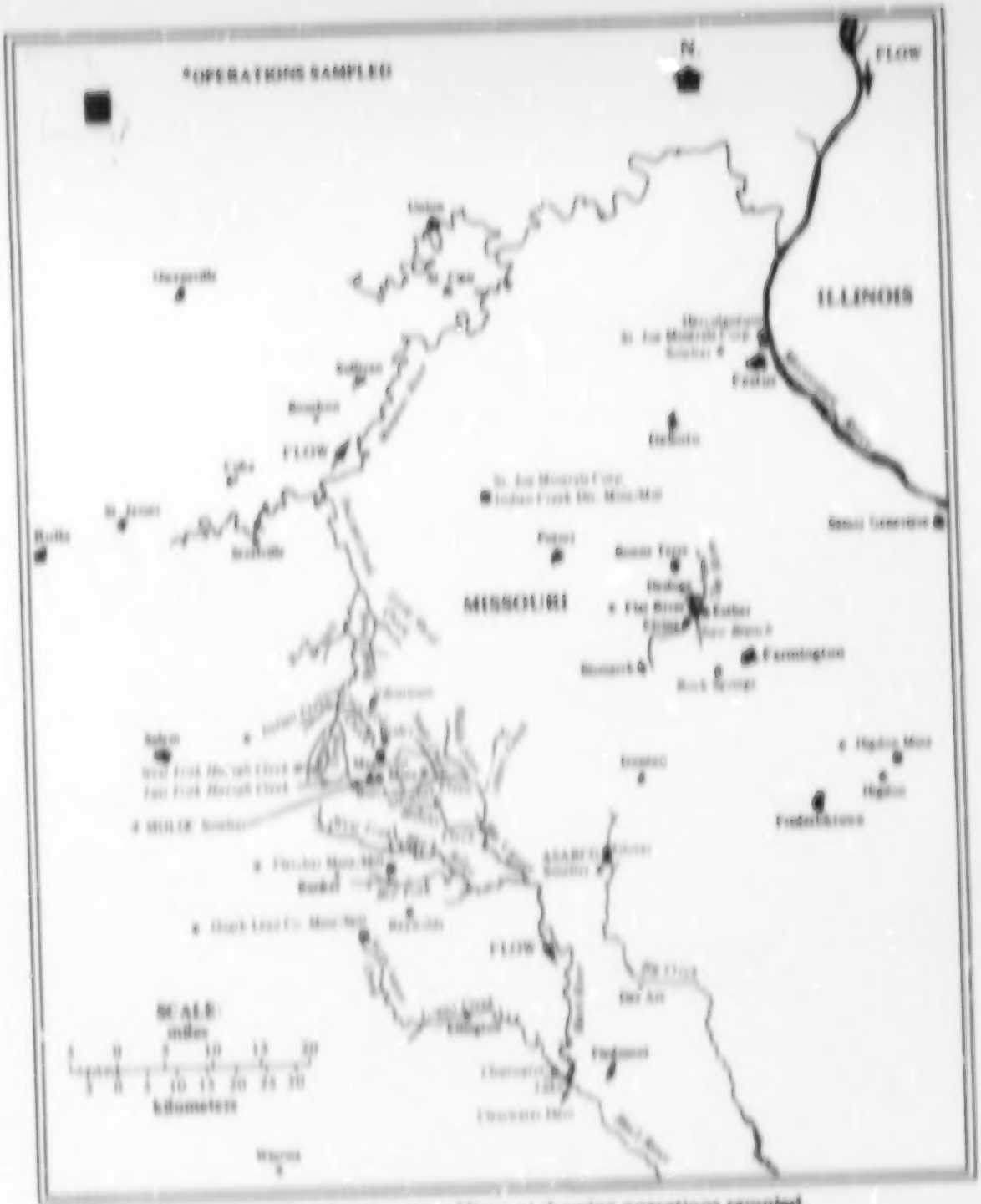


Figure 20. Southeastern Missouri showing operations sampled and associated features discussed in text.

The New Lead Belt runs over 56 km (35 miles) north-south through the virtually uninhabited Ozark Plateau in Clark National Forest. A regional fracture trend in the Cambrian Bonneterre dolomite bedrock controls the occurrence of narrow caverns. These caverns extend 360 meters (1200 feet) below the surface down to the underlying insoluble pre-Cambrian granite basement and have been gradually filled by reductive precipitation from circulating groundwater with up to 270 meters (900 feet) of sulfide ore. The sulfide ores are of massive galena (PbS) with a thin rim of sphalerite (ZnS) and chalcopyrite ($CuFeS_2$) containing a small amount of argentite (Ag_2S). The first chalcopyrite ($CuFeS_2$) containing a small amount of argentite (Ag_2S). The first mines at Viburnum, geophysically discovered, were opened in 1967 and the trend has become the largest lead-producing district in the world. The production required by the terms of Forest Service leases, coupled with recent restrictions on pigment and gasoline use, have cut the price of lead drastically.

A mine must pump 315 to 440 liters/second (5000 to 7000 gallons/minute) of groundwater to operate. Conventional operations run most of this relatively clear water through the mill and flotation concentrators to wash away waste rock flour. The high grade of the more massive galena ore often overloads the flotation system, and, with the decline of lead prices, it is not economical to recover the last percent or more of the lead mined.

The muddy water, organic flotation agents, and wastes are discharged into any convenient nearby valley which could be provided by a series of dams made of the coarser mill tailings (by a cruder version of the cyclone separation process described for the White Pine facility). The final effluent thus varies with the pond size and mine water volume discharged.

The dark lead-bearing dolomite mud coats the stream bottoms with a gray algal-bacterial slime. The benthic fauna appeared to be intolerant of this lead-rich diet. The entire region is drained by various tributaries of the Mississippi River.

The air and water pollution by Pb, Zn, Cu, and Mn are being studied on a continuing basis by B.G. Wixson and colleagues in Environmental Engineering at the University of Missouri-Rolla, with support furnished by the National Science Foundation RANN Program.

Viburnum--The most extensive producer in the area is the St. Joe Minerals Corp. This Corporation was the largest producer from the Old Lead Belt 48 km (30 miles) to the east. Conventional mines and mills were in operation at Viburnum and at the Fletcher Mine/Mill, and under construction on the intervening Brushy Creek. Their ponds were minimal in size, the dams were eroding rapidly, and the effluent from their plants was virtually abiotic, apparently due to excess organic flotation agents discharged. The milled ore was shipped to the old company smelter on the Mississippi at Herculaneum. All of their active facilities were sampled.

Two mines at Viburnum were in operation along Indian Creek, a tributary of Huzzah Creek, which is a tributary of the Meramec River. The ore from the downstream mine was trucked up to the mill at the upstream mine. The truck route, paralleled by a large-diameter pipe which conveyed the mine water to the upper pond, was built along the creek. Samples were taken from the relatively clear uppermost pond (which has a thick mat of the algae Chara); from the lower pond; from mill tailing discharge; and from the creek below the lowermost dam, which contained mill wastes. Analyses of lead and cadmium in water, mud, and biota are given in Table 21.

Bisby Region--The largest facilities center around the Homestake Mining Co./American Metals Climax, Inc. (Missouri Lead Operating Co., or MOLOC smelter, 1.2 km (0.75 mile) southwest of the Magmont Mine, midway between Bisby and Buick). Its slag is presently being stockpiled, although it was used on roads until recently. The effluent is combined with tailings from their Buick mill and the Magmont mine/mill of COMINCO American (Kennecott Copper and partners), settled, recirculated, and discharged into Strother Creek. The large volume of mine water from this huge operation fills Strother Creek over capacity. (Much larger pond capacity would be required to allow evaporation of this flow. Separation of the tailings, however, and recirculation of the mill water required could be achieved readily, as suggested to MOLOC by Wixson).

TABLE 21. CONCENTRATIONS OF HEAVY METALS (ppm) NEAR VIBURNUM, MISSOURI

Sampling Location	Cadmium	Lead
Mine/Mill Tailing Discharge	← Pumped from Mine →	
Water	2.5	1200
Mud	None	None
Algae	--	--
Minnows	--	--
Pond 1		
Water	0.008	4.3
Mud	<1.3	500
Algae (Chara)	1	61
Minnows	--	--
Pond 2		
Water	0.001	0.55
Mud	2.5	--
Algae	None	None
Minnows	--	--
Waste Discharge into Indian Creek		
Water	0.001 0.002	0.04 0.9
Mud	--	300
Algae	None	None
Minnows	--	9

Samples were taken of slag and tailings at the MOLOC/Magmont complex. Effluent, sediment, and biota samples were taken below the final serpentine spillway (designed by Wisson to promote algal growth) above Asher Cemetery. Results of chemical analyses are given in Table 22. The analysis shows 0.27 ±0.05 ppm Pb in this water. Wisson found up to 0.53 ppm Pb in the water at this point and approximately 60 ppm Pb, 7-14 ppm Zn, 0.25-0.7 ppm Cd, and 5-7 ppm Cu in Strother Creek mud. Control samples were taken along Neals Creek, which joins Strother Creek below the last MOLOC dam.

Significant Tl was not found in the plant effluent or river samples. Tl levels determined by plant laboratory personnel from emission spectroscopy were clearly below 1 ppm in any waste stream. Serious Pb pollution occurred due to the slag-granulating cooling water, which must be recirculated to meet current effluent standards.

TABLE 22. CONCENTRATIONS OF HEAVY METALS (ppm) NEAR BIXBY, MISSOURI (MOLOC/MAGMONT COMPLEX)

Sampling Location	Cadmium	Lead
Clean Control Streams		
Water	≤0.003	≤ 0.013
Sediment	0.5	50
Algae	0.14	20
Larvae (Caddis)	1.7	44
Crayfish	0.29	6.7
Minnows	--	2.8 ± 4
Magmont Mill		
Water	0.003	5
Sediment	15	1000
Algae	None	None
Larvae (Caddis)	None	None
Crayfish	None	None
Minnows	--	None
MOLOC Smelter		
Water	None	None
Sediment	8.2	10,000
Algae	None	None
Larvae (Caddis)	None	None
Crayfish	None	None
Minnows	--	None
Strother Creek		
Water	0.001	0.27
Sediment	0.6-1.8	850-2000
Algae	0.19-0.21	None
Larvae (Caddis)	3.4	920 (Blockfly)
Crayfish	2.6	48
Minnows	--	5.8

Bunker Region--A mine and mill operated by the Ozark Lead Co. (a subsidiary of Kennecott Copper) in the most isolated location (southeast of Bunker) has the most nearly complete recirculation system yet in the trend. A small, nearly abiotic effluent discharged into Sweetwater Creek was sampled, and 1 ppb Cd and 44 ppb Cu were found.

The most serious waste problem is the effluent from the Fletcher mine/mill close to Bee Fork. The settling ponds are narrow and already full of tailings, except for the small, shallow lagoons in the floodplain. The virtually abiotic effluent into Bee Fork was sampled along with the upstream control biota. The effluent was sampled where mixing first occurs (Figure 26) and 3.2 km (2 miles) further downstream. The effluent contained 0.12 ± 0.003 ppm of lead by atomic absorption analysis. Recent severe local flooding had reduced the benthos all along Bee Fork, which receives flash runoff from a cleared area upstream (south) around the small town of Bunker. Analyses of lead and cadmium in water, sediments, and biota are given in Table 23.

TABLE 23. CONCENTRATIONS OF HEAVY METALS (ppm) NEAR FLETCHER MINE/MILL, MISSOURI (ST. JOE MINERALS CORP.)

Sampling Location	Cadmium	Lead
Bee Fork		
Above Outfall*		
Water	0.001	<0.01
Sediment	0.5	200
Algae (Myriophyllum)	None	None
Larvae (Caddis)	2.2	11
Crayfish	0.12	10
Minnows	0.25	22
Mill Tailing Pond		
Water	0.001 0.002	0.12 0.13
Sediment	--	--
Algae (Myriophyllum)	0.29	112
Larvae (Caddis)	2.6	71
Crayfish	None	None
Minnows	None	None
Below Outfall		
Water	0.001	0.003
Sediment	1	58
Algae (Myriophyllum)	0.5	19
Larvae (Caddis)	1.6	97
Crayfish	0.22	19
Minnows	0.08	3.9

*Below Highways, Lilly Farm, and Bunker

Figure 25. Tailings effluent at Bee Fork Creek.

In summary, the lead levels in waters from the New Missouri lead belt were high, as shown in Tables 21 and 23. The low levels of lead discharge which can be achieved were shown below the Viburnum mine/mill, which recirculates its water through two tailing ponds. In the final effluents, lead was below 10 ppb, zinc below 100 ppb, and cadmium below 1 ppb. Only copper (44 ppb) was above the levels in uncontaminated control streams. Cadmium values were all low.

Missouri Old Lead Belt (St. Francois Mountains Trend)--

Summary--St. Joe Minerals Corp. and ASARCO have extensive facilities in the Old Lead Belt on the Bonneterre outcrop in the St. Francois Mountains, where lead has been known to exist since the 18th century.

Flat River--Near the confluence of Shaw Branch with the Flat River, at the towns of Flat River and Esther, there are extensive mining wastes. In the river, there is a mountain of coarse, gravel-size tailings which is over 92 meters (300 feet) high and contains visible galena. On the branch, the closed St. Joe Federal mine and mill are surrounded by extensive waste piles and tailing ponds. To determine the effects of both waste sources, samples were collected at the confluence. Analyses of water, slag, sediment, and biota for lead and cadmium are given in Table 24.

Glover--The ASARCO Custom smelter on Big Creek near Glover, Missouri, has been recently rebuilt. It serves Ozark Lead Co. and some of the remaining minor production from the Old Lead Belt. Water is recirculated at this smelter. The slag effluent and sediment were sampled, and water from Big Creek was sampled above and below the small effluent discharge, which contained 53 ppb Cd, 220 ppb Pb, 212 ppm Zn, and 5 ppb Tl. (Refer to Table 24).

Herculaneum, Missouri--

The St. Joe smelter was built in 1864 on a narrow terrace between high cliffs and the Mississippi River. Its capacity is being increased by high-rise construction. The hot effluent, including sanitary sewage and acid-plant leakage, is discharged directly into the main deepwater channel of the river from a new tail structure. A water recirculating system has been "under construction" for years. The slag and river above the smelter were sampled, but access to the present effluent could not be obtained. The St. Joe Minerals Corp. slag piled along the bank of the Mississippi River at Herculaneum, contains from 1 to 3.5% lead, 1 to 9.2% zinc, 300 to 3800 ppm copper, and 14 to 250 ppm cadmium. The most toxic of this material was being bulldozed into the river in large quantities in the process of building a sanitary sewage treatment plant next to the smelter.

TABLE 24. CONCENTRATIONS OF HEAVY METALS (ppm) NEAR FLAT RIVER (ST. JOE MINERALS CORP.) AND GLOVER (ASARCO)

Sampling Location	Cadmium	Lead
North of Flat River, 300 ft high Tailing Pile		
Water	None	None
Slag	None	None
Sediment	1.3	12,000
Algae	None	None
Larvae	None	None
St. Joe Federal Mill Near Flat River		
Water	Closed	Closed
Slag	None	None
Sediment	7.5	1600
Algae	None	None
Larvae	None	None
Drainage into Shew Branch at Flat River		
Water	0.001	0.23
Slag	None	None
Sediment	1.3	6600
Algae	0.98	2800
Larvae (Caddis)	2.1	2200
ASARCO Glover Smelter		
Water	0.053	0.22
Slag	12	9600
Sediment	300	25
Algae	1130	2230
Larvae	None	None
Drainage into Big Creek		
Water	< 0.001	0.013
Slag	None	None
Sediment	--	--
Algae	--	--
Larvae	--	--

East St. Louis, Illinois--

The American Zinc (now owned by AMAX) electrolytic refinery, sampled in November 1973, is located in the floodplain of the Mississippi River. Spent acid and water were discharged into a serpentine lagoon discharging into a slough. This waste and two tank-bottom sludges (one being rich in Cu) dumped on its banks were sampled. The cupriferous waste was 12% zinc, 15% copper, 0.18% lead, and 0.62% cadmium. The black sludge covering a large area west of the plant was 8.7% zinc, 0.75% copper, 0.45% lead, and 0.1% cadmium. No thallium was detectable at the 90-280 ppb level.

White Pine, Michigan--

The Copper Range Co., White Pine, Michigan, mine and smelter, with a large tailing area, is on the Mineral River draining into Lake Superior, cleanest and coldest of the Great Lakes (Figure 27). These waters still support commercial fisheries and provide the public supply for tens of millions of people. The wastes and waters from the smelter and mill were sampled down to the lake on August 24-26, 1973.

In the copper processing at White Pine, pit-run shale is milled to a mud and most of the CuS concentrate floated off with surfactants. The fine tailings from the mill are neutralized with lime and piped to storage behind earthen dams. The storage area is gradually covering the large region between the mine and Lake Superior. Some of the coarser tailings are used to build the dam and fill the mine. Mill water, rain, and snowmelt are decanted with minimal mud (restricted by state standards) and collected in Native Creek (Figure 28), a deep stream 1 to 2 meters (3 to 6 feet) wide, which joins the Mineral River where it is 15 meters (50 feet) wide and 0.3 meter (1 foot) deep, just above Lake Superior.

The wet concentrate from the mill is melted in reverberatory furnaces. Up until now, pyrite has been added to enhance sulfur concentration and reduce smelting costs. This pyrite has been acquired from Bethlehem Steel's Cornwall, Pennsylvania, mine, which also supplies the Sparrows Point, Maryland acid plant. Because the pyrite deposits are nearly exhausted, and in an effort to reduce sulfur emissions from the stack, the concentration of pyrite used in the White Pine processing is currently being minimized and, presumably, will be eliminated.

For this reason, the nature of the slag and the water effluents is now in a state of transition. In any case, slag from the furnaces is dumped, crushed, washed, and (as much as possible) sold for road and other use. Wash water and other smelter runoff settles in a small new pond and flows through the woods and Bannister Creek (1 to 2 meters (3 to 5 feet) wide), into the Mineral River (Figure 29), where it is 4 meters (12 feet) wide and 1 meter (3 feet) deep, just below the Carp Lake Township dump.

The survey of the Mineral River (Figure 27) started above the smelter and company town, where it is 0.3 to 0.6 meter (1 to 2 feet) wide and has a complete normal boreal biota consisting of algae, aquatic moss, caddisfly larvae, water striders, and minnows. The river was then followed past the facilities, including a sewage treatment plant and uncontrolled erosion from the slag pile, down to the junctions with the muddy influents.

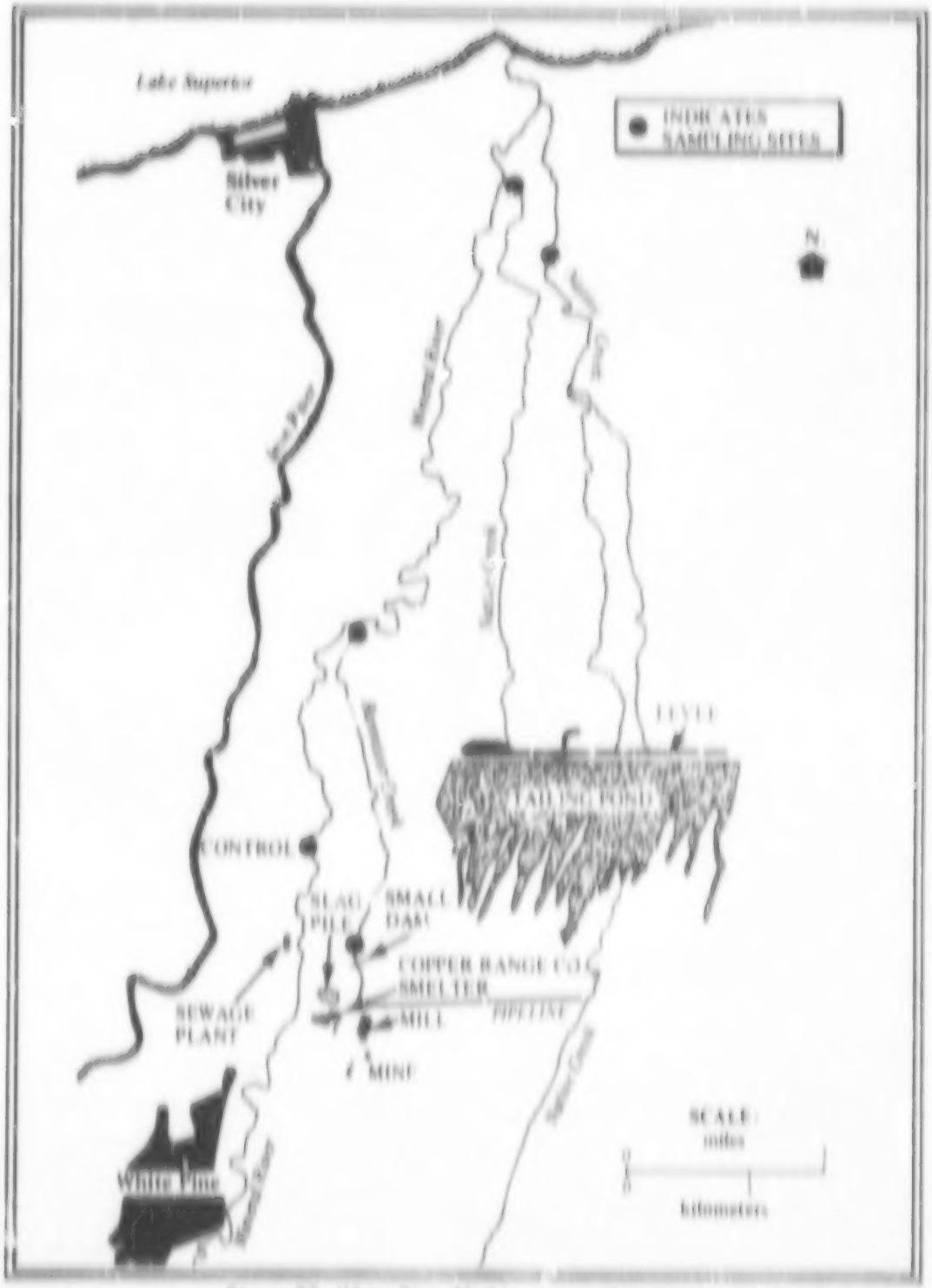


Figure 37. White Pine, Michigan, sampling sites.

Figure 28. Native Creek (White Pine, Michigan).

Figure 29. Turbidity of Bannister Creek near junction of Mineral River (White Pine, Michigan).

With the assistance of plant environmental-control personnel, we sampled soil, tailings, pond waters, and effluent into both Native and Bannister Creeks. Results of these analyses are given in Table 25. The mud in the Mineral River below Bannister Creek continues out into Lake Superior to such an extent as to reduce the biota to a few algae and water striders. The latter probably feed primarily on terrestrial insects which fall in from the forest.

No thallium was detected, even in recycled flue dusts. Significant levels of lead, copper, and zinc are present.

TABLE 25. CONCENTRATIONS OF HEAVY METALS (ppm) NEAR WHITE PINE, MICHIGAN (COPPER RANGE CO., AUGUST 1972)

Sampling Location	Cadmium	Lead	Copper	Zinc
Control (Mineral River below [North of] Sewage Plant)				
Sediment	0.067	11	240	22
Algae	0.73	45	360	81
Larvae (Caddis)	---	---	---	---
Fish (Stickleback)	1.0	30	66	66
Mill Tailings (Native Creek) at Tailing Pond Outfall				
Sediment	0.14	0.69	6600	Not analyzed
Algae	3.0	128	6000	1800
Larvae (Caddis)	---	---	---	---
Fish (Stickleback)	11	73	380	190
Mill Tailings (Native Creek) at Junction of Mineral River				
Sediment	0.068	0.08	1800	15
Algae	0.88	24	63	---
Larvae (Caddis)	11	190	230	300
Fish (Stickleback)	None	None	None	None
Slag Runoff (Bannister Creek) at Dam Outfall				
Sediment	0.19	0.93	1300	180
Algae	None	None	None	None
Larvae (Caddis)	None	None	None	None
Fish (Stickleback)	None	None	None	None
Slag Runoff (Bannister Creek) at Junction of Mineral River				
Sediment	0.011	0.19	1300	67
Algae	None	None	None	None
Larvae (Caddis)	None	None	None	None
Fish (Stickleback)	None	None	None	None

Eastern U.S.

Perth Amboy and Sewaren, New Jersey:

A visit was made to Perth Amboy, New Jersey, to examine plants typical of those situated on estuaries and tidal basins. It was found that the ASARCO and Anaconda copper refining plants on the Raritan River estuary discharge into an area containing 4 hectares (10 acres) of waste (Figure 30). Next to ASARCO along Arthur Kill, National Lead reclaims battery plates along with other operations, with over 20 hectares (75 acres) of waste placed directly in the tidal marsh of the estuary. While none of its own operations may contribute Tl to the aquatic ecosystem, the dump was also used by surrounding industry and is believed to be a serious source of pollution, possibly including Tl. Waste-material samples were obtained for the Anaconda refinery. Samples were also taken at the Copper Pigments and Chemical Works, Inc., located at Sewaren, New Jersey.

Analyses of the collected samples were made using the Perkin Elmer Model 303 atomic absorption spectrometer. The results of these analyses are listed in Table 26. They are consistent with the amounts of thallium present in primary blister copper and the sludge-handling techniques of electrolytic refining. However, the Cottrell-precipitator dusts, which contained more hazardous concentrations, were only intermittently discharged to the aquatic environment.

The high thallium concentrations found in New Jersey were from small dumps of sludge and other highly toxic material, which may not be representative. They were not resampled, however, because of the high level of background contamination throughout the entire industrial area, including the Raritan River and Arthur Kill, which drain these sites.

TABLE 26. RESULTS OF THALLIUM ANALYSES FOR NEW JERSEY SAMPLES

Plant	Location	Sample	Thallium Concentration (ppm)
Anaconda Co.	Perth Amboy	Sludge Dump, near tailing pond	20
Anaconda Co.	Perth Amboy	Sludge Dump, fresh	21
Anaconda Co.	Perth Amboy	Sludge Dump, gley horizon	28
Copper Pigments and Chemical Works	Sewaren	Sludge Dump	17

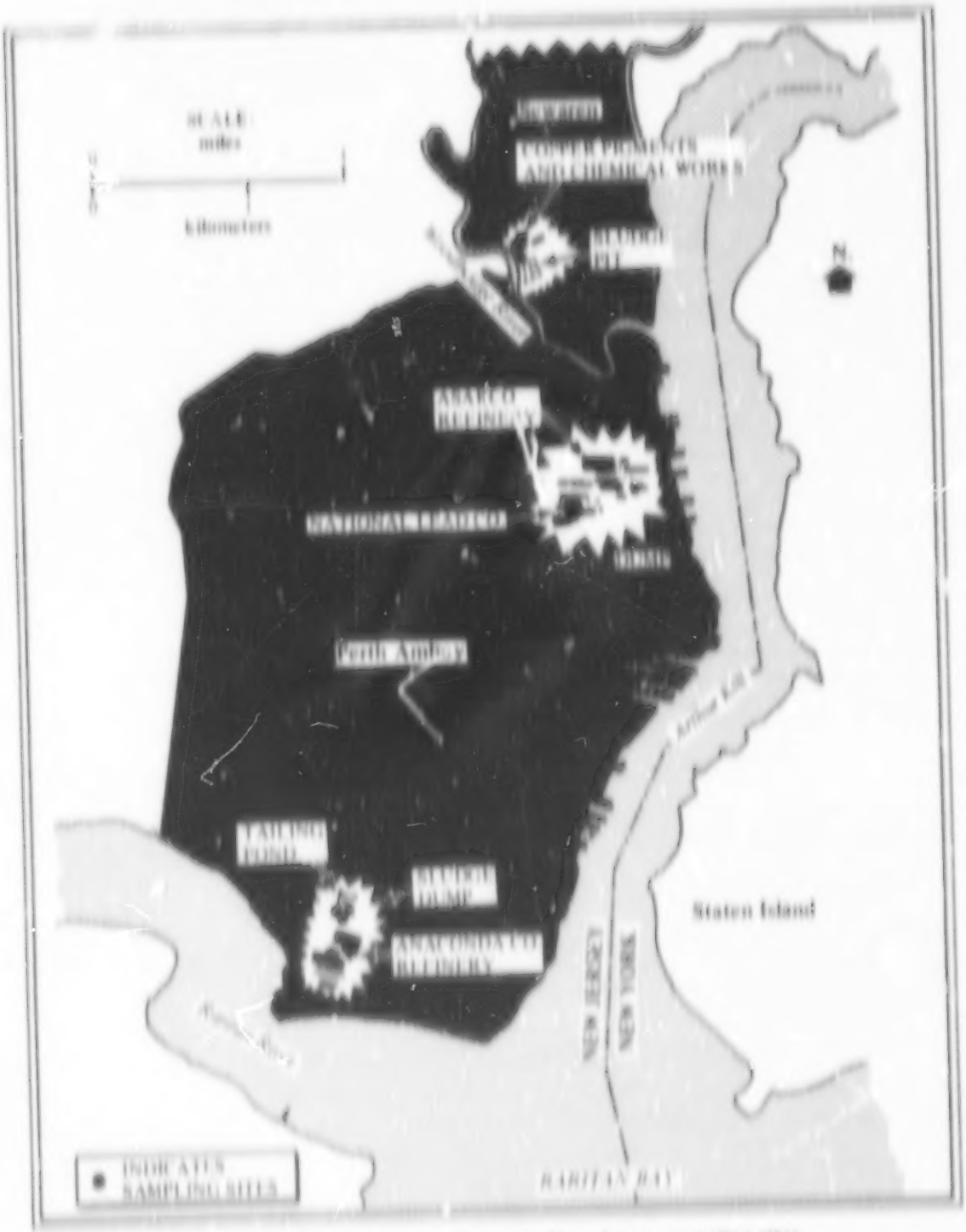


Figure 30. Perth Amboy/Sewaren, New Jersey, sampling sites.

Palmerton, Pennsylvania--

The old smelter and refinery complex of the New Jersey Zinc Co. is at Palmerton, Carbon County, Pennsylvania, on the Lehigh River just above the watergap through Blue Mountain where the river emerges from the Appalachian Mountains (Figure 31). Metal fumes from the low stacks at Hazard (West Palmerton) have killed almost all of the trees in the valley. Hot 30°C (87°F) effluent (pH 4.5) from the smelter was sampled where it enters the Lehigh River along with slag and the resistant flora: algal slimes, mosses, and horsetails. Mud in the river bed contained 13% zinc, 500 ppm copper, 0.13% lead, and 5.4 ppm cadmium. The river was heavily polluted by sewage from Lehighton, Jim Thorpe, and other communities above the smelter.

The acid plant and refinery in East Palmerton are on Aquashicola Creek, which joins the Lehigh at the watergap. Cold effluent and sediment were sampled from the outfall at the creek, where acid recovery appears to be satisfactory. The water contained only 90 ppb zinc. The sediment in the creek, however, contained 6.1% zinc, 0.7% copper, 200 ppm lead, and 93 ppm cadmium.

Other Known Thalliferous Sulfide Accumulations

Sites Not Requiring Sampling or Impossible to Sample--

The high-capacity plant in the Salt Lake City, Utah, area (Garfield and Tooele) drains directly into Great Salt Lake, which is essentially a lifeless, saturated brine.

The known Tl reserves in the dump at Mercury, Utah (4), are not near any permanent water and drain through ephemeral channels into dry Rush Lake. Inactive and secondary plants were not sampled, although the locations of a number of such waste concentrations are known.

The zinc smelter operated by the Matthiessen and Hegeler Zinc Company in the village of Spelter (0.4 km (0.25 mile) south-southwest of the town of Meadowbrook), West Virginia, 7.2 km (4.5 miles) north-northeast of the city of Clarksburg, has apparently filled an entire bend in the West Fork River up to 6 meters (20 feet), over 0.8 km (0.5 mile) long, of what was floodplain. High rainfall of the region tends to promote leaching. The river, like most of those in the Coal Measures, is entrenched without a wide floodplain, so catastrophically high water levels may occur. However, the river is too polluted to provide significant data on bioconcentration.

Lithopone production has become negligible. A small amount has recently been exported to South Vietnam. Lead-free ZnO has replaced it domestically. The largest plant (American Zinc Company) at Columbus, Ohio (which also produces sulfuric acid), is not situated on a surface stream. Any surface runoff apparently runs into a nearby cemetery and percolates into the soil.

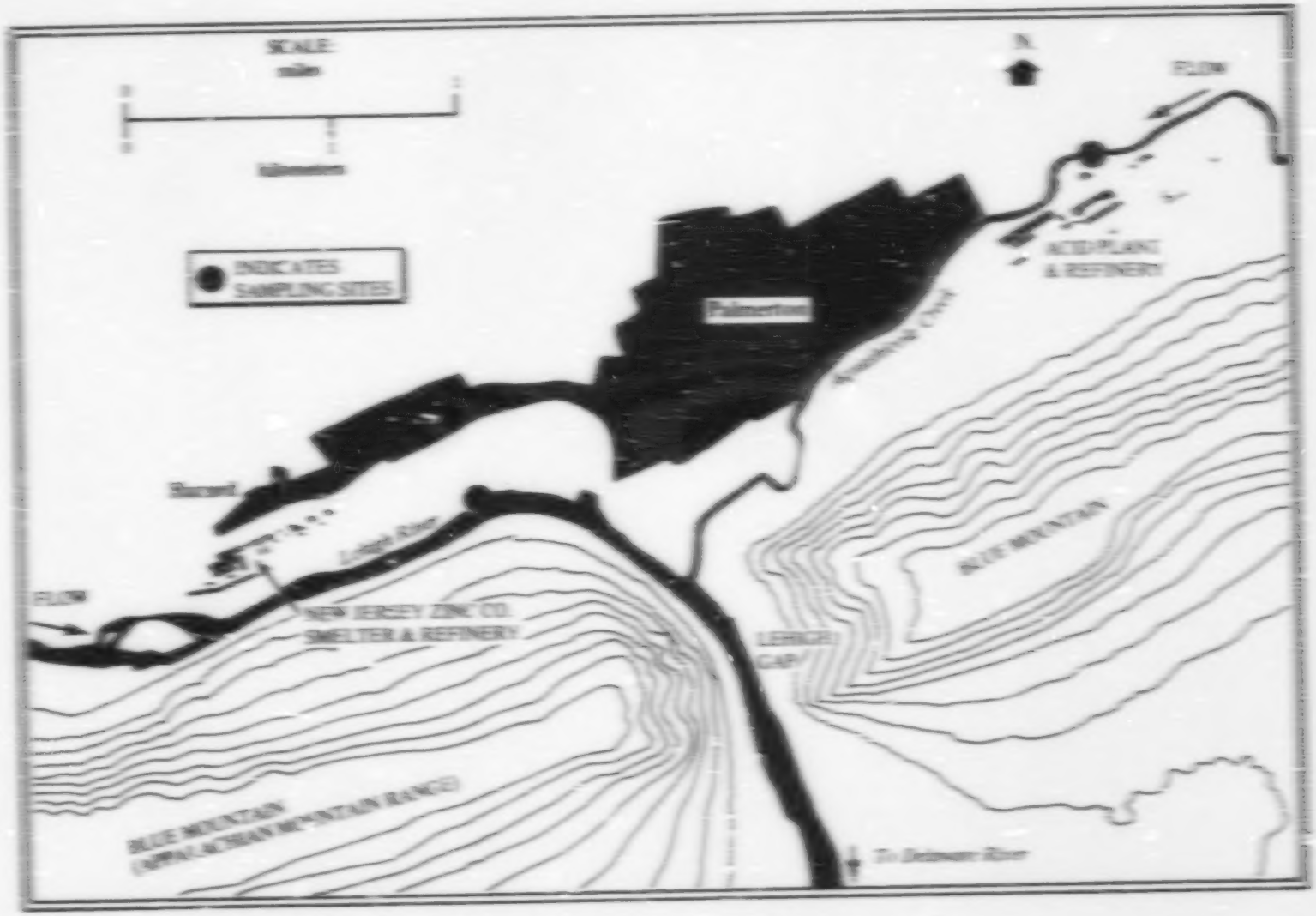


Figure 31. Palmerton, Pennsylvania, sampling site.

Steel Mills in Bethlehem, Pennsylvania, and Elsewhere--

Blast furnaces formerly using anthracite coke at the main Bethlehem Steel Co. plant in Bethlehem, Pennsylvania, are closed. Current metallurgical operations use electrical furnaces to produce high-grade specialty steels. The slag dump and Lehigh River water at this plant were sampled. Analysis of these and other steel slags previously sampled indicates that ferrous metallurgy produces little serious heavy-metal hazard. No thallium was detected. The gross observable biological effects are negligible compared with those of copper, lead, and zinc operations.

Sulfuric Acid Plant in Copper Basin, Tennessee--

Up to 3-1/2% Tl has been reported in sulfuric acid made from thalliferous pyrite (5). Sulfuric acid made from pyrite (FeS_2) may concentrate Tl in the exit stack gas. The original Cottrell precipitator was installed to remove sulfuric acid mist at the ASARCO copper smelter in Selby, California, in 1909. A decision was made to sample from the Copperhill smelter and acid plant within the large Copper Basin region of Tennessee.

The Copper Basin (Figure 32) is an eroding, devegetated wasteland, 9.6 km (6 miles) across, centered near Ducktown, Polk County, and covering the southeast corner of Tennessee. Chalcopyrite, pyrite, and other sulfides similar to the rocks mined at Kellogg, Idaho, and White Pine, Michigan, are found in black schists of the Ocoee series. Mines are scattered throughout the basin, with an active mill and abandoned smelter at Isabella (Ducktown) on North Potato Creek and an active smelter with a large acid and chemical plant at Copperhill on the Ocoee River.

The control sampling stations for this region were the headwaters of Burra-Burra Creek above the tailing pond and the Ocoee River at the Tennessee-Georgia border (Figure 32). A number of areas suspected of heavy metal concentration were sampled. These included ore from an abandoned mine pit near the tailing pond, the tailing pond itself, drainage from the tailing pond into North Potato Creek, the Copperhill smelter wasteweir on Davis Mill Creek and a ditch (West Newton) draining through the vicinity of the smelter to the Ocoee River. The Ocoee River was further sampled below the Rogers Bridge and 8 miles downstream at the Ocoee No. 3 powerhouse. Results of analyses are given in Table 27.

The tailing pond was found to contain 1.4 ppm phenol, apparently from chemical wastes in the mill water. Relatively large amounts of thallium are stored in the tailing pond as a byproduct of pyrite mining and sulfuric acid production. The tailing pond is subject to flood overflow. Cd could not be detected anywhere in the Ocoee River water or uncontaminated control stream waters but was found in all the outfalls and creeks leading from the mill and smelter. Copper, zinc, lead, and cadmium showed a tendency to accumulate in aquatic roots and mosses but not in algae and fish. This probably results from direct exchange between sediments and root hairs.

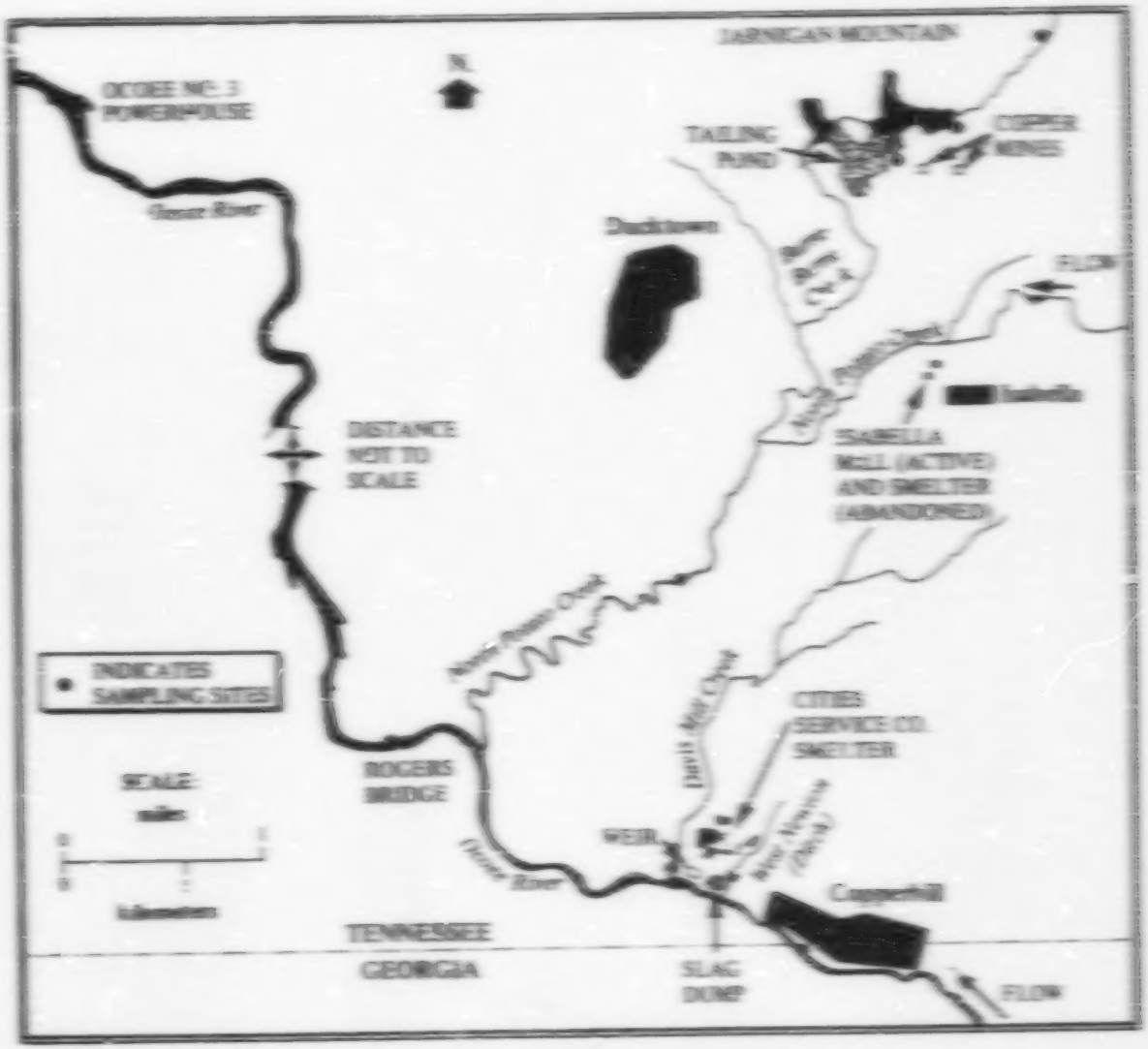


Figure 32. Copper Basin, Tennessee, sampling sites.

TABLE 37. CONCENTRATIONS OF HEAVY METALS (ppm) IN COPPER BASIN, TENNESSEE REGION

Sampling Location	Thallium	Cadmium	Lead	Copper	Zinc
Controls					
Headwaters of Burra Burra Creek at Jernigan Mountain (pH 5.6)					
Water	<	<0.002	<0.00	<0.01	0.10
Sediment	0.1	0.1	<10	50	25
Aquatic Roots	<	0.25	<5	5	0.5
Algae	<	None	None	None	None
Minnows	<	None	-	-	None
Upstream Ocoee River at George Gate Ling (pH 5.0)					
Water	<	<0.003	<0.00	<0.01	0.1
Sediment	<	0.4	70	30	200
Aquatic Roots	<	0.1	<110	230	0.40
Algae	<	0.4	80	75	230
Minnows	<	0.5	-	-	90
Contaminated Materials					
Mine Waste Near Tailing Pond					
Water	<	0.---	None	None	None
Sediment	0.05	7	200	2100	600
Aquatic Roots	<	None	None	None	None
Algae	<	None	None	None	None
Minnows	<	None	-	-	None
Tailing Pond					
Water	<	0.007	<0.00	0.01	0.10
Sediment	1.4	7.0	200	2100	10,000
Aquatic Roots	<	0.15	6.2	6.2	15
Algae	<	None	None	None	None
Minnows	<	None	-	-	None
Pond Drainage into N. Potato Creek (pH 5.5)					
Water	<	0.003	0.2	0.09	1.0
Sediment	<	-	-	-	-
Aquatic Roots	<	None	None	None	None
Algae	<	None	None	None	None
Minnows	<	None	-	-	None
Copperhill Smelter Waste Weir on Davis Mill Creek (pH 2.9)					
Water	<	0.003	1.0	4.0	0.5
Sediment	<	7	170	2000	300
Aquatic Roots	<	None	None	None	None
Algae	<	15.00	None	None	None
Minnows	<	None	-	-	None
W. Newton Ditch (at gate) (pH 3.9)					
Water	<	0.008	0.1	0.01	0.5
Sediment	<	10	180	980	120
Aquatic Roots	<	None	None	30.00	None
Algae	<	None	None	None	None
Minnows	<	None	-	-	None
Ocoee River below Rogers Bridge (pH 6.7)					
Water	<	<0.003	0.2	0.02	0.5
Sediment	0.9	10	2500	2000	1000
Aquatic Roots	<	1.0	600	400	400
Algae	<	30.00	None	None	None
Minnows	<	None	-	-	No ID
Ocoee Power, upst at Ocoee No. 3 Powerhouse (pH 6.6)					
Water	<	<0.003	<0.02	0.08	0.05
Sediment	<	1	140	1000	1000
Aquatic Roots	<	0.20	<1.0	25	<1
Algae (Aquatic Moss)	<	0.5	60	240	194
Minnows	<	None	-	-	None

Ore from an abandoned mine pit near the tailing pond contained 11% copper, along with 900 ppm zinc, 300 ppm lead, and 1.3 ppm cadmium. The slags at Isabella and Copperhill vary from 500 to 1400 ppm copper, 350 to 4800 ppm zinc, 75 to 200 ppm lead, and 0.5 to 1 ppm cadmium. Thallium was not detectable at the 100 ppb level in any of these samples. Thallium was not detected (at a sensitivity of 1 ppb) in any water or biota samples collected from this region.

Anthracite-Burning Powerplants Near Scranton and Hazleton, Pennsylvania--

Some coal deposits, notably anthracite of high-temperature diagenetic origin, contain considerable amounts of thallium associated with pyrite. In addition to any small amount of heavy metals in the original biomass of the coal swamp, as groundwater slowly circulates through the sediment mass, the reducing effect of the coal traps metal ions as sulfides. The more deeply buried the coal, the more pyrite (FeS_2) and other sulfides crystallize within the fossil biomass and the greater the trapping potential for heavy metals. The sequence of burial changes that occurs in coal can be expressed in the fixed-to-volatile carbon ratio, essentially the graphite present relative to the amount of hydrocarbons (organic precursors decay relatively rapidly to stable hydrocarbons and CO_2). These metamorphic changes are the result of increased temperature at depth. Therefore, anthracites are most likely to contain significant metal concentrations. When this coal is burned at power plants, any Tl present can become concentrated in electrically precipitated fly ash. Power plants using this type of coal are now restricted to the original mining district from the Lehigh River to Scranton (centered on Wilkes-Barre), Pennsylvania. Up to 76 ppm of thallium has been reported in flyash (6).

On the basis of these arguments, the anthracite region of Pennsylvania was selected for study of the heavy metal hazard in fuel burning. Unfortunately, earlier low coal prices has caused closing of most mines, and, consequently, almost all anthracite-burning operations. Electric powerplants sampled are identified in Table 28, and their locations are shown in Figure 33. All but the standby plant at Harding were sampled. No other large anthracite-consuming processes were found in use locally.

TABLE 28. ANTHRACITE-BURNING POWER PLANTS (PENNSYLVANIA)

Status	Plant/Owner	Location
Stand-by	Pennsylvania Power & Light Co.	At Harding on Susquehanna River
Closed	Pennsylvania Power & Light Co.	At Harris Dam on Nesquehoning Creek
Ruined	Glen Alden Coal Co.	At Nanticoke on Susquehanna River
	Glyphont	At Dickson City on Lackawanna River
Buried Under Waste	Jenkins	At Port Blanchard on Susquehanna River

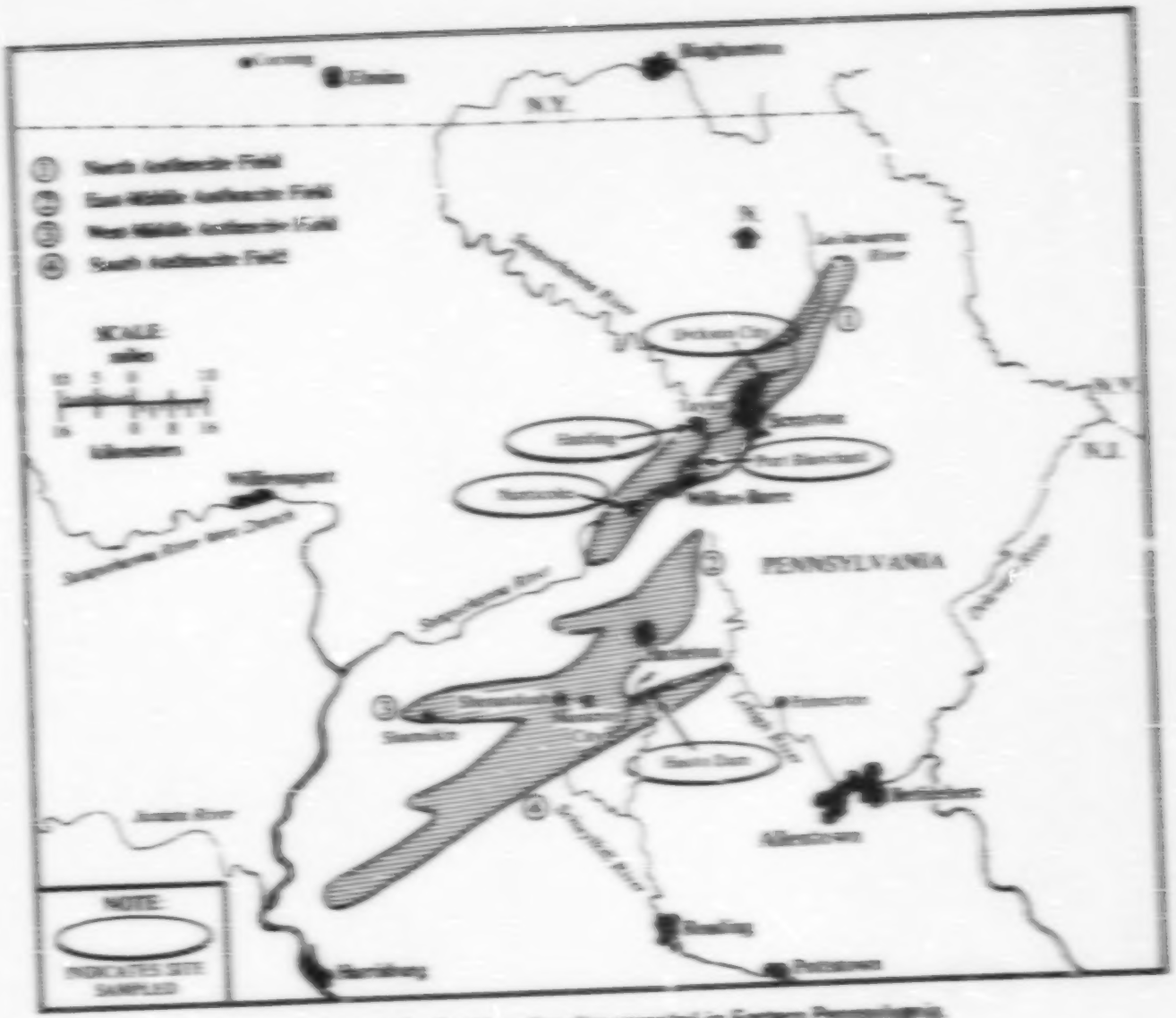


Figure 23. Coal-burning sites sampled in Eastern Pennsylvania.

Ash from the closed power plant at Hauto Dam contained 47 ppm zinc, 37 ppm copper, 0.51 ppm lead, 21 ppb cadmium, but no measurable thallium. Strip-mine tailings in the immediate vicinity contained comparable amounts of heavy metals. Flyash from the abandoned Glen Alden power plant on the Susquehanna River at Nanticoke contained 64 ppm zinc, 123 ppm copper, 2 ppm lead, 0.26 ppm cadmium, and no measurable thallium.

Mine-run coal contains larger amounts of waste each year, and the convenient surface area available for disposal becomes less. Huge mountainous piles of waste fill the coal-bearing valleys. In the narrow southern valleys, conveyors pour the waste over the rimrock and down into the surrounding unpolluted wooded plateau. The fine tailings of silt or "slush" have also been deposited in huge unstable piles to avoid the final cost of returning it underground or to fill strip-mine pits. The mud eroded from the mound of waste at Port Blanchard contained 170 ppm zinc, 40 ppm copper, 0.41 ppm lead, and 77 ppb cadmium.

As much as 36 metric tons (40 short tons) of water were dumped from the mines into streams to recover each ton of coal. The streams draining waste and strip areas were acid and dead. Particularly dirty stream water from Taylor, southwest of Scranton, was sampled, as well as sediment from several waste ponds and streams. The water contained 71 ppb copper and 89 ppb zinc. No cadmium, lead, or thallium were detected.

All of the data indicate that coal mining and burning could contribute significant quantities of toxic lead and cadmium to the environment by flood erosion. However, no measurable thallium quantities would be contributed.

Bituminous-Coal-Burning Powerplant at East Corning, New York--

For comparative purposes, a bituminous-coal-fired powerplant in East Corning, New York (Figure 34), was sampled. The plant is on the Chemung River, a large, swift Appalachian stream with a steep gradient and a coarse alluvial bed.

The river water and bed were sampled immediately above and below the plant. Fine sediment and benthos (algae, mayfly larvae, and miscellaneous forms) were obtained from beneath many boulders. Fish, including minnows, foot-long suckers, and giant shiners, were netted by hand from swift, shallow riffles.

A flyash pond, approximately 92 meters (100 yards) from the river bank and backwater, was sampled to determine the variability of the fine metalliferous waste. This material erodes into the Chemung River as a result of rainfall and washwater leaching. Smartweed (Equisitum), and poplar (Populus) seedlings were found growing close to the flyash pond. The recent flood, which did even more serious damage in the Anthracite Coal District, washed out the Corning city sewage treatment plant just above our sample sites. In addition to the increasing upstream pollution, the flood washed away everything around the powerplant, including much flyash and its treatment system.

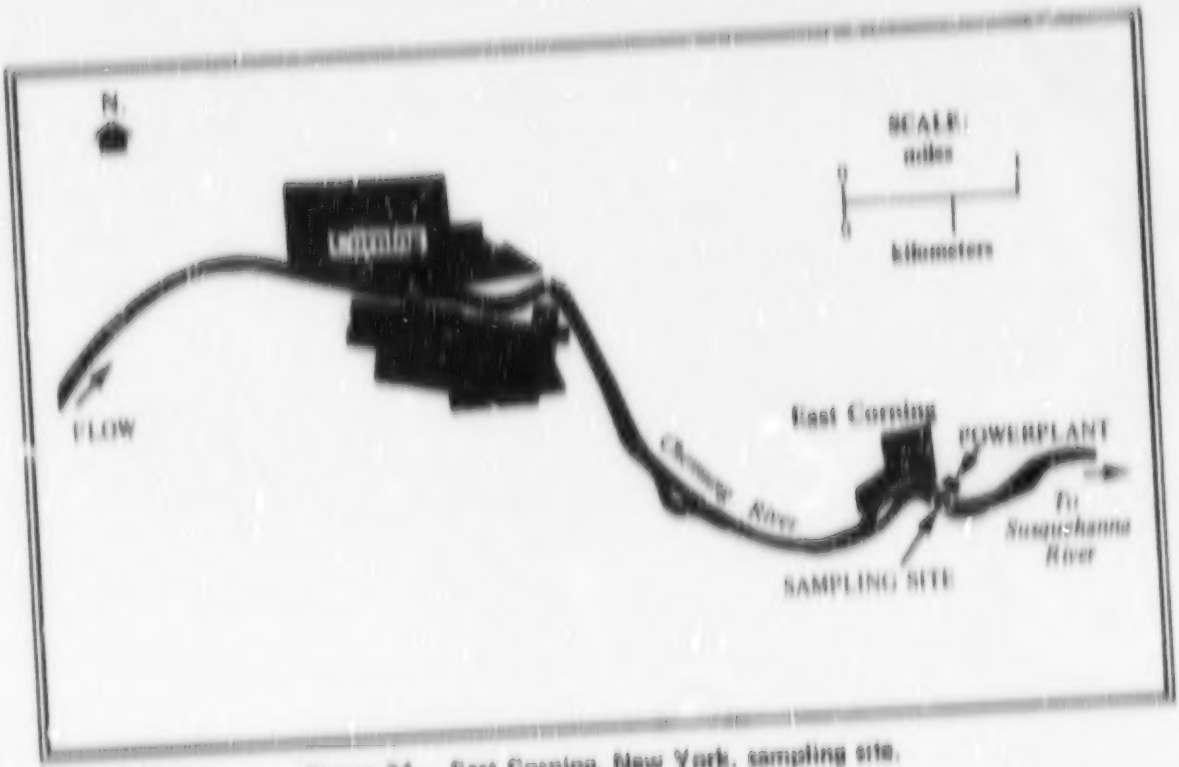


Figure 34. East Corning, New York, sampling site.

Results of heavy metal analyses for water, sediment, and biota samples are tabulated in Tables 29 and 30. Although significant thallium was found in sediments and biota, none was detected in water samples. The data suggest that bituminous-coal pyrite does not contain enough Tl to provide an environmental threat. Cadmium, copper, lead, and zinc were found in sediments, biota, and water. Levels of cadmium and lead in river water both upstream and downstream of the flyash pond exceeded recommended EPA drinking water standards (EPA lead limit-0.05 mg/l; cadmium limit-0.10 mg/l). The data indicate that the flyash pond could be a source of cadmium and lead discharges to the river.

TABLE 29. RESULTS OF EAST CORNING, NEW YORK, WATER SAMPLE ANALYSES (ppm)

	Cadmium	Copper	Lead	Zinc
Downstream river water	0.017±0.002	0.039±0.002	0.13±0.01	0.036±0.004
Upstream river water	0.015±0.002	0.007±0.002	0.084±0.009	0.015±0.002
Upstream river water	0.018±0.002	0.008±0.002	0.10±0.01	0.010±0.001
Upstream river water	0.022±0.002	0.008±0.002	0.12±0.01	0.018±0.002
Fly ash pond	0.018±0.002		0.33±0.02	0.14±0.01
Fly ash pond (duplicate)	0.10±0.01	0.11±0.01	0.27±0.03	0.14±0.01
Fly ash pond (triplicate)	0.017±0.002	0.031±0.003	0.14±0.1	0.048±0.005
	<0.002	0.002±0.002	<0.002	<0.002
No thallium was detectable in water samples				

Variations shown are estimated analytical errors from variations in standard signal levels.

TABLE 30. RESULTS OF EAST CORNING, NEW YORK, SEDIMENT, VEGETATION, AND BIOTA SAMPLE ANALYSES (ppm)

	Copper	Lead	Thallium	Zinc
Fly Ash Pond:				
Horsetails	27 ± 3	23 ± 2	<2	39 ± 4
Poplar	29 ± 3	20 ± 2	1 ± 1	67 ± 7
Grass-leaves	22 ± 2	18 ± 2	<1.2	32 ± 3
Grass-roots	16 ± 2	40 ± 5	1.6 ± 0.9	11 ± 1
Grass-leaves & Roots	20 ± 3	11 ± 1	<1.3	29 ± 4
Helianthus	18 ± 2	2.1 ± 0.8	1.5 ± 0.8	26 ± 3
Fine Sediment	20 ± 1	21 ± 2	1	120 ± 10
Fine Sediment (duplicate)	14 ± 1			22 ± 2
Coal	28 ± 3	1.	1.9 ± 0.9	63 ± 6
Septic Sediment	29 ± 3		6.2 ± 1	
Cladophora	8.2 ± 0.8	12 ± 1		30 ± 3
Coarse Sediment	13 ± 1	2.2 ± 0.4		26 ± 3

ECOLOGY OF THALLIUM

Purpose of This Subsection

The ecology of most of the trace metals measured in this study (copper, zinc, lead, and cadmium) has been discussed in detail previously in the scientific literature. Their known biological and geochemical balances are reasonably well supported by the data in this report. Thallium (along with some data on indium), however, has rarely been studied and is considered in more detail.

Abundance and Distribution of Thallium

There is approximately 1 gram of thallium (Tl) per ton of the earth's crust. This is one-tenth the abundance of lead and 1/306 that of copper and zinc. Thallium is strongly concentrated in igneous and volcanic rocks (4).

Significant amounts of Tl are concentrated in the high-temperature sulfide metal deposits of volcanic terrains. In the United States, these are bodies that are restricted to Alaska, the western Cordilleran mountain states, and the Appalachians. Although the distribution of Tl within such ores is variable (depending on the composition of the mineralizing solutions, country rock, and geothermal gradient), it has been possible to indicate which industrial plants present the greatest Tl hazard as long as volcanic-origin ores are processed.

Tl is usually associated with sulfide concentrations of zinc (Zn), lead (Pb), copper (Cu), iron (Fe), cadmium (Cd), arsenic (As), indium (In), selenium (Se), and tellurium (Te). The overt mineralization of Tl is summarized in Table 31. The solutions, minerals, and equilibrium of Tl deposition with Cd, Zn, Cu, and Fe can be visualized by means of the Eh-pH diagram, a plot of reduction-oxidation potential (Eh) versus acity (pH) (see Figure 35). The appropriate Eh versus pH field depicts the equilibrium thermodynamic conditions under which Tl can exist in solutions and solids.

TABLE 31. THALLIUM MINERALS

Name	Chemical Composition	Occurrence
Crookesite	$(Cu,Tl,Ag)_2Se$	A Variety of Argentite (Silver Glance, Ag_2S)
Lorandite	$TlAsS_2$	With Realgar, AsS
Hutchinsonite	$(Tl,Ag)_2S \cdot PbS \cdot 2As_2S_3$	In Dolomite, $MgCa(CO_3)_2$
Vrbaite	$Tl(As,Sb)_3S_5$	With AsS, As_2S_3, and HgS

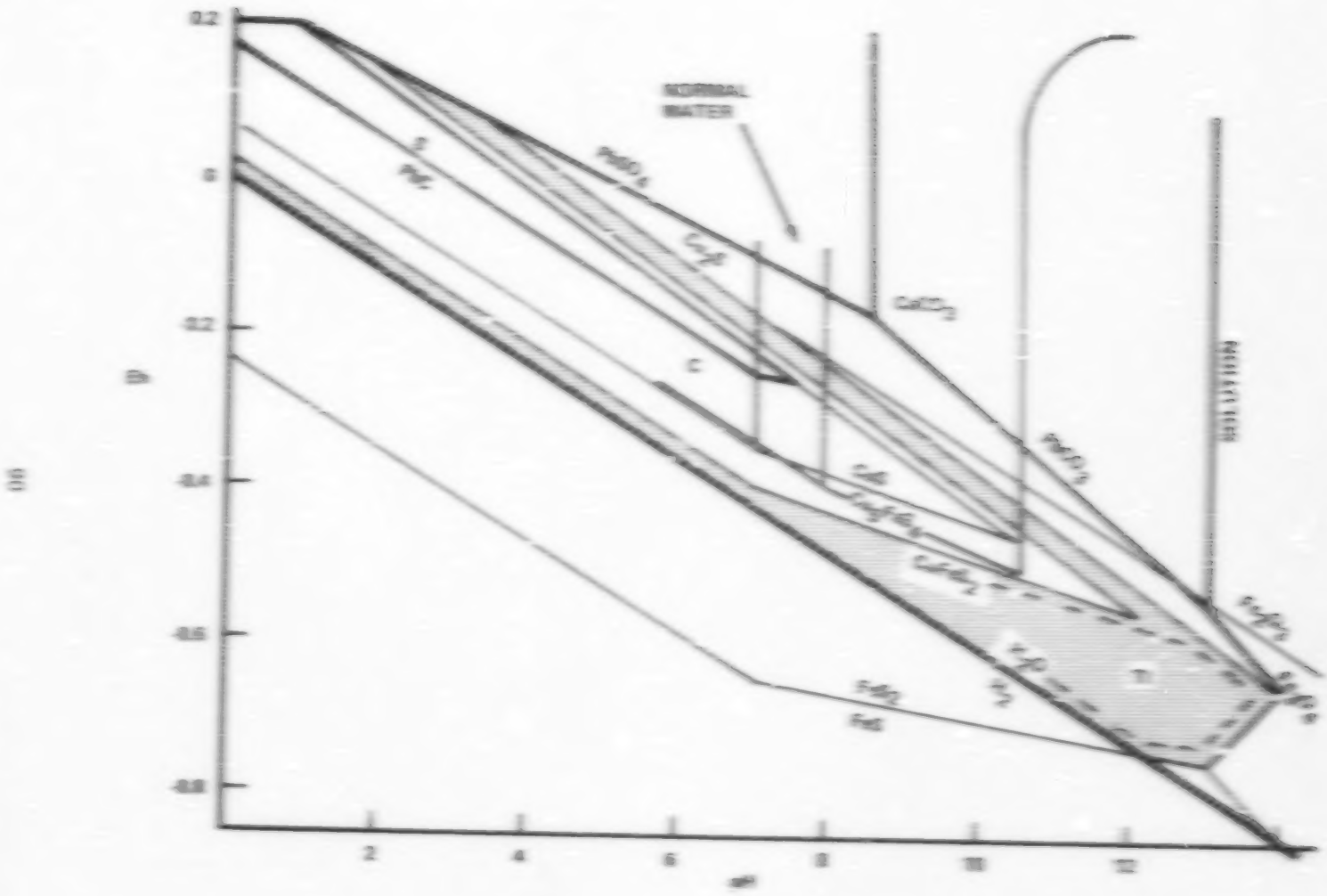


Figure 35. Chemical environments of metal deposition.

The Eh-pH ranges of Tl deposition are shown as the shaded area in Figure 35. Depositions from hot brine (H_2O) occur in the field including Tl and chalcopyrite ($CuFeS_2$), pyrite (FeS_2), and galena (PbS), but not magnetite (Fe_3O_4) or chalcocite (Cu_2S). Eh-pH diagrams are available for the systems Cd-Fe-S-O-H and Pb-S-CO_2-O-H, shown superposed in Figure 35. The deposition of Tl is confined to the FeS_2 field. Zn and Cd are similar to Pb.

Thus, the most important occurrence of the Tl is in pyrite, or "fool's gold," which is almost universally present in base-metal ores, coal, and other chemically reduced rocks.

Copper is, by far, the most important sulfide metal commercially. Its most important ore, chalcopyrite ($CuFeS_2$), like FeS_2, can contain relatively large quantities of Tl.

The western copper mines occur in a trend from Arizona through Utah and Nevada to Butte, Montana, paralleling the Pacific Coast. Up to 5% Tl is found in cupriferous pyrites (5).

Lead and zinc are found associated with or to the east of the Cordilleran copper belt. The more easterly occurrences are of colder origin and tend to contain less Tl. The zonation of commercial major metal from west to east (from high- to low-temperature deposition) is roughly Fe-Cu-Au-Ag-W-Mo-Zn-Pb (7).

The forms of the trace metals found in mining and smelting wastes are indicated below.

Tailings, which contain most of the pollution from metal mining, are mineralogically the same (primarily sulfide) as the ore which has been concentrated. Smelter slag, however, is fayalite (Fe_2SiO_4) with other unrecovered heavy metals substituted for iron in the lattice.

The major precipitant for toxic metals in natural waters is carbonate. The beneficial effect of carbonate alkalinity for removing soluble metals from water is particularly well-demonstrated in the Missouri New Lead Belt, particularly Strother Creek, which receives large quantities of mill and smelter lead discharges (5 ppm in mill water, 1550 ppm in mill sediments, and 10,500 ppm in smelter sediments). The high carbonate bedrock in Strother Creek precipitates lead effectively from the water to 0.27 ppm. The tie up of lead and cadmium in sediments does not prevent uptake by biota in this case, however, as evidenced by high concentrations of lead in larvae and crayfish, which feed on the metal-laden detritus.

As discussed under analytic methods, chloride ions form a significant control to the solution transport of thallium. A particular halogen complex (ligand) is formed with the thallous ion, which is readily adsorped or precipitated. The loss of this ligand is similar to the precipitation of thallium with bromine outlined in Appendix B.

Sulfate ions have a slight solubilising effect on thallium as compared to nitrate ions at constant pH, probably due to the oxidation of some Tl^{+} to more soluble Tl^{+3}.

Chelation by dissolved organic substances may be an important mechanism, in addition to the thallous chloride complex and adsorption on particulate matter, particularly in suspended clays with their enormous surface area. This is especially true in streams like the South Fork of the Coeur d'Alene River, which is saturated by untreated sewage. The organic ligands generally tend to increase metal solubility, in contrast to the chloride precipitation effect.

Behavior of Thallium in Natural Waters

The chemistry of thallium in natural waters has some puzzling features. The most obvious is the discrepancy between the relative abundance in soils (typically up to 10 ppm in those derived from granite crust) and the rarity in sea water (normally less than 0.01 ppb as reported by Rex and Goldberg (8). The atomic radius of Tl^{+} is 0.144 nanometers, making the density relatively low so that Tl is carried into stack gas where it is easily precipitated electrically. Up to 9% Tl has been found in flue dusts (4). Soil thallium is derived from orthoclase, the common potash feldspar where Tl^{+} may readily substitute for K^{+} in the lattice because of comparable atomic size (0.144 vs. 0.133 nanometers, respectively).

Thallium Exchange with a Montmorillonite Clay

Need for the Experiments:

It was hypothesized that the substitution of thallium for other metallic cations may take place in the montmorillonitic clays, which, if true, could be a significant factor in minimizing thallium movement in the environment. To check this hypothesis, a series of experiments was designed in which a montmorillonitic clay (hectorite) was chosen to determine the extent of preference of exchange of the thallous ion compared to the potassium ion and to other ions such as copper and zinc.

Montmorillonite is the principal clay mineral of bentonite beds, which originate from altered volcanic ash. Montmorillonite minerals are common as alteration products of igneous and metamorphic rock minerals in an alkaline environment with little leaching (e.g., arid climates). The western U.S. Rocky Mountain region has an abundance of montmorillonite in its soils. There are different species in the montmorillonite group, and they vary in the type and degree of isomorphous lattice substitution rather than in structure. In this study, the montmorillonite called hectorite (hectorite #34 - API reference standard) was used. This mineral is one in which the principal substitutions are octahedral and has a general structural formula of:

$$(Al_{.01}\ Li_{.30}\ Mg_{2.67})\qquad (Si_4)\ O_{10}\ (OH)_2$$

In the presence of water, the cations in the interlayer positions may be easily exchanged with other cations when available in solution. Isomorphous substitution results in charge deficiency, which may occur in the octahedral or tetrahedral layer. The charge deficiencies can be neutralized by exchangeable cations so that the mineral becomes electrically neutral. Therefore, exchange may occur not only by cations in the interlayer position, but in layers of the lattice as well.

Approach--

Ten- and one-gram samples of hectorite per liter distilled water were prepared containing 1000, 100, and 10 micrograms per liter of thallium (I), copper (II) and zinc (II). The pH of the solution of hectorite and water was adjusted to 4 and approximately 8 with dilute sulfuric acid prior to the addition of metals. The clay slurry was continually agitated for 24 hours to achieve good contact between the clay and metal ions in solution. After the contact period, clay was removed by settling and centrifuging to obtain a clear liquid prior to extraction and atomic absorption analysis.

The liquid, free of clay, was extracted with DDC (diethyldithiocarbamate) to concentrate the metal ions. Thallium analysis was performed using a heated graphite atomizer, whereas copper and zinc were aspirated directly.

Blank samples without hectorite and hectorite solutions without metals were prepared to assure no interferences or metal losses.

Results--

Three separate experiments were carried out using hectorite, potassium-treated hectorite, thallium, copper, and zinc in various concentrations. Ten grams of hectorite per liter of water with different concentrations of thallium, copper, and zinc at two pH levels (4.0 and 8.2) revealed more efficient takeup of metal ions in basic solution. (Refer to Table 32). At pH 8.2, the thallium concentration was reduced from 1000 micrograms per liter to 25 micrograms per liter. Copper and zinc were reduced from 1000 micrograms per liter to less than 10 micrograms per liter. Other concentrations of Tl, Cu, and Zn were reduced to below their detectability limit.

In acidic solution (pH 4.0), metal reduction in solution was not as pronounced as in basic solution. Initial 1,000-microgram levels of Tl, Cu, and Zn were reduced to 900, 562, and 619 micrograms per liter, respectively. Concentration of metals at 100 micrograms per liter also did not reduce as dramatically as in basic solution but did adsorb in greater proportion than the 1000-microgram-per-liter metal sample at the same pH value.

An experiment was performed in which the concentration of clay was changed from 10 grams of hectorite per liter to 1 gram of hectorite per liter of solution at a pH of 8.1 (Table 33). Initial concentrations of 1000-micrograms-per-liter levels of Tl, Cu, and Zn were reduced to 115, 270, and 511 micrograms per liter, respectively. Other concentrations

TABLE 32. EXCHANGE CAPACITY OF HECTORITE WITH THALLIUM, COPPER, AND ZINC (10 g/liter HECTORITE)

pH	Initial (μg/l)			Final (μg/l)		
	Thallium	Copper	Zinc	Thallium	Copper	Zinc
8.2	1000	1000	1030	95	<10	<10
8.2	100	100	100	<3	<10	<10
8.2	10	10	10	<1	<10	<10
8.2	0	0	0	<1	<10	<10
4.0	1000	1000	1000	900	982	919
4.0	100	100	100	3	10	10
4.0	10	10	10	<1	<10	<10
4.0	0	0	0	<1	<10	<10

TABLE 33. EXCHANGE CAPACITY OF HECTORITE WITH THALLIUM, COPPER, AND ZINC (1 g/liter HECTORITE)

pH	Initial (μg/l)			Final (μg/l)		
	Thallium	Copper	Zinc	Thallium	Copper	Zinc
8.1	1000	1000	1000	115	970	911
8.1	100	100	100	3	<10	<10
8.1	10	10	10	<1	<10	<10
8.1	0	0	0	<1	<10	<10

of metals (100- and 10-microgram-per-liter levels) were reduced near or below their detectable limit.

When hectorite initially is saturated with 2000 micrograms per liter potassium, the rate of exchange for thallium is only slightly affected (Table 34), a reduction of 1000 to 25 micrograms per liter was obtained without potassium ions, and a reduction of 1000 to 90 micrograms per liter was obtained in a potassium-treated clay. The concentrations of copper and zinc in solutions of clay saturated with and without potassium ion were reduced to below their detectability.

TABLE 34. EXCHANGE CAPACITY OF POTASSIUM TREATED HECTORITE WITH THALLIUM, COPPER, AND ZINC

pH	Initial (μg/l)				Final (μg/l)		
	Potassium	Thallium	Copper	Zinc	Thallium	Copper	Zinc
8.2	2000	1000	1000	1000	90	<10	<10
8.2	2000	100	100	100	4	<10	<10
8.2	2000	10	10	10	<1	<10	<10
8.2	2000	0	0	0	<1	<10	<10

Conclusions--

The experimental results show that thallium ions can be removed effectively from solution by a montmorillonite clay. Greater removal of thallium is achieved in slightly basic waters versus slightly acidic waters. This may be due to the increased solubility of the metallic ion in acidic media. Other metal ions--specifically, copper and zinc--also follow the same trend. Clays, saturated with potassium ions, show only slight differences to clay that had not been treated with potassium ions.

The disappearance of thallium from less-acid waters may be related to reduction of unstable Tl^{+++} (thallic) to Tl^{+} (thallous) ions and subsequent ion-exchange with suspended clay. This mechanism is quite efficient, and there is little biological uptake of thallium. However, organic complexes such as those formed with MIBK are known on analysis and may persist through the food chain despite their toxicity. The general path of thallium from water through biota is shown in Figure 36. A good example is the South Fork of the Coeur d'Alene River, mentioned above (Table 9).

The metal fractionation between water and sediment can be understood in terms of the solubility of the available salts of the metal ions found (Table 35). Tl, like Pb, accumulates from acid water in neutral or alkaline sediments, especially fine muds.

TABLE 35. SOLUBILITIES OF SELECTED HEAVY METAL SALTS IN WATER

Heavy Metal (Ion)	Solubility of Salt in Neutral (pH 7.0) water at 20°C (68°F)* (ppm (mg/l))			
	Carbonate	Chloride	Sulfate	Sulfide
Thallium^{+++}	Does not exist	853,000 (17°C)	Decomposes	Insoluble
Thallium^{+}	43,000 (15.5°C)	3,900 (15.5°C)	48,700	220
Cadmium^{++}	Insoluble	1,400,000	760,000 (0°C)	1.3 (18°C)
Lead^{++}	1.1	9,900	42.5 (25°C)	0.86 (18°C)
Copper^{++}	(Basic) Insoluble	707,000 (0°C)	143,000 (0°C)	0.33 (18°C)
Copper^{+}	Insoluble	62	Decomposes	0.0 (18°C)
Zinc^{++}	10 (15°C)	4,320,000 (20°C)	965,000	0.9 (18°C)

*Unless temperature is otherwise indicated. 0°C = 32°F; 15°C = 59°F; 17.5°C = 80°F; 17°C = 63°F; 18°C = 64°F; 25°C = 77°F.

Data based on information given in Weast, Robert C. (ed.), Handbook of Chemistry and Physics, 53rd Edition (1972-1973), The Chemical Rubber Company (Cleveland, Ohio) and Lange, Norbert A. (ed.), Handbook of Chemistry, Revised Tenth Edition (1967), McGraw-Hill Book Company (New York).

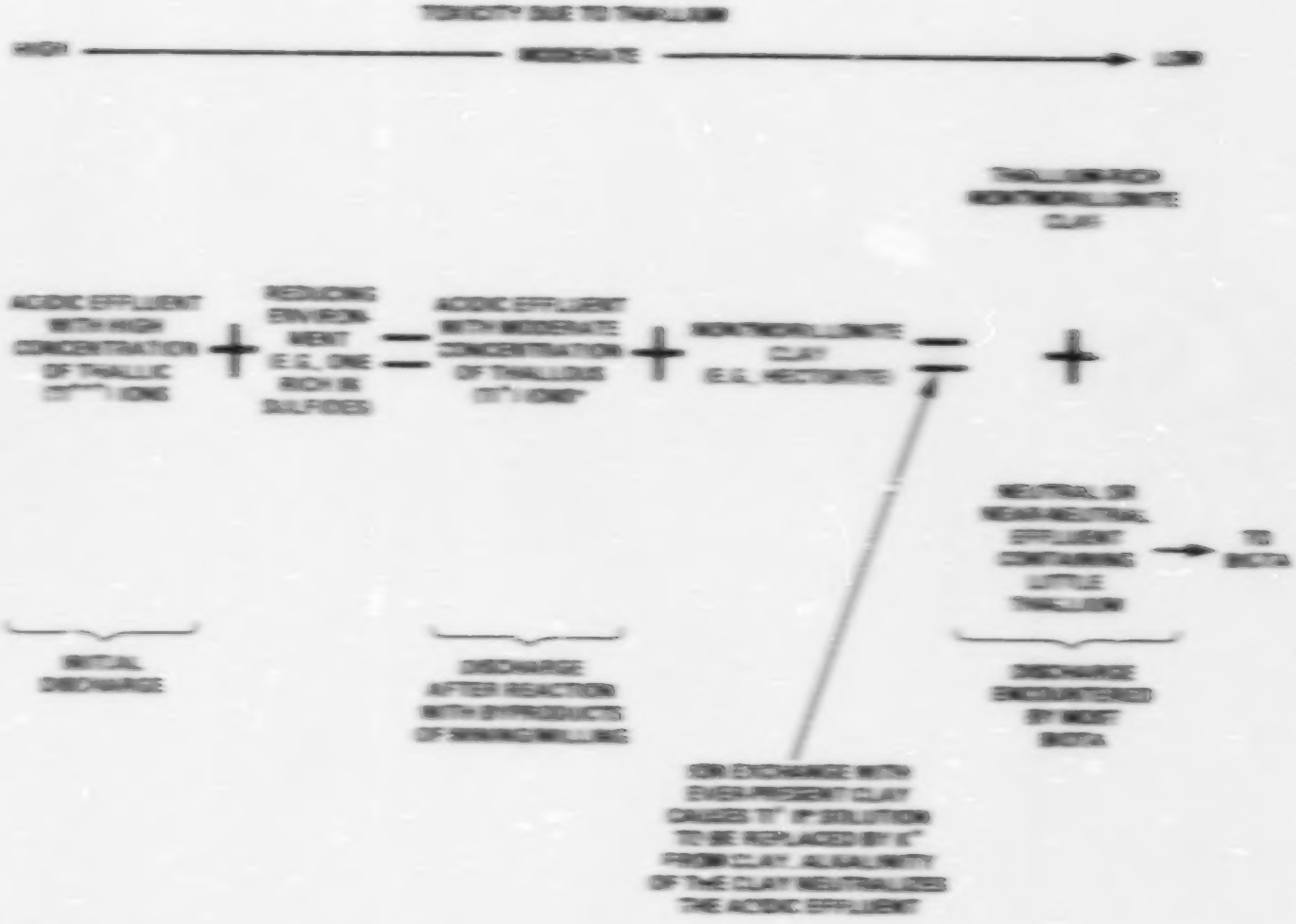


Figure 36. Generalized flow of acidified thallium in the environment.

Biological Concentration of Thallium

The relations of the more toxic metal (Tl, Cd, Pb) concentrations in each trophic level of the biota to its sediment and water concentrations are plotted in Figures 37 through 40. Data from all sampled sites are included. The concentration of metal in the biota was found to be more closely related to the concentration in its bottom sediment than to its concentration in water except for a few floating algal slimes surviving above lead-rich mud, particularly at East Helena. Toxic water discharges can occur sporadically, leaving a record in the sediment. Generally, benthic organisms were found to accumulate more than fish.

In the following discussion, prior observations (9) for each metal are summarized for comparison with the data collected in this study. The average concentration of cadmium found in rivers by Hoger was 0.24 ppb, but only 0.11 ppb in seawater. In rivers, the average concentration of lead is now 4.2 ppb, and in surface seawater, 0.5 ppb, primarily due to leaded gasoline. Deeper seawater contains only 0.03 ppb. Toxicity is cumulative and varies from 100 ppb for oysters to 4 ppm for fish. The average concentration of copper in rivers is 10 ppb, about as much as in nearshore seawater. Copper is toxic to algae at approximately 25 ppb, although fish can tolerate 30 ppm. The average concentration of zinc is 10 ppb in rivers and up to 15 to 20 ppb in seawater. Aquatic toxicity of zinc requires 5 to 10 ppm. Marine plankton can concentrate heavy metals at factors which can vary from 910 for cadmium, 4100 for lead, and 20,000 for zinc (9).

The higher trophic levels sampled in this study, especially larvae and fish, were found to have lower concentrations of toxic metals than lower trophic levels (algae). We believe this is due to a combination of factors including feeding on uncontaminated detritus, mobility and biochemical rejection mechanisms.

This agrees with Merlini et al. (10), who showed copper concentrations of 2.2 ppm in Lake Maggiore algae (Myriophyllium), but only 0.9 ppm in small fish (Alburius) and 0.5 ppm in large fish (Coregorus, Scardinius). Zinc decreased from 20 ppm in algae to 4 to 8 ppm in large fish.

Unlike methyl mercury, thallium and other toxic heavy metals showed little increase in concentration up the food chain. Sulfide precipitation removes these readily reduced cations, concentrating them in black organic oozes.

The graphs (Figures 37 through 40) summarize the research in showing that there was little bioconcentration from water.

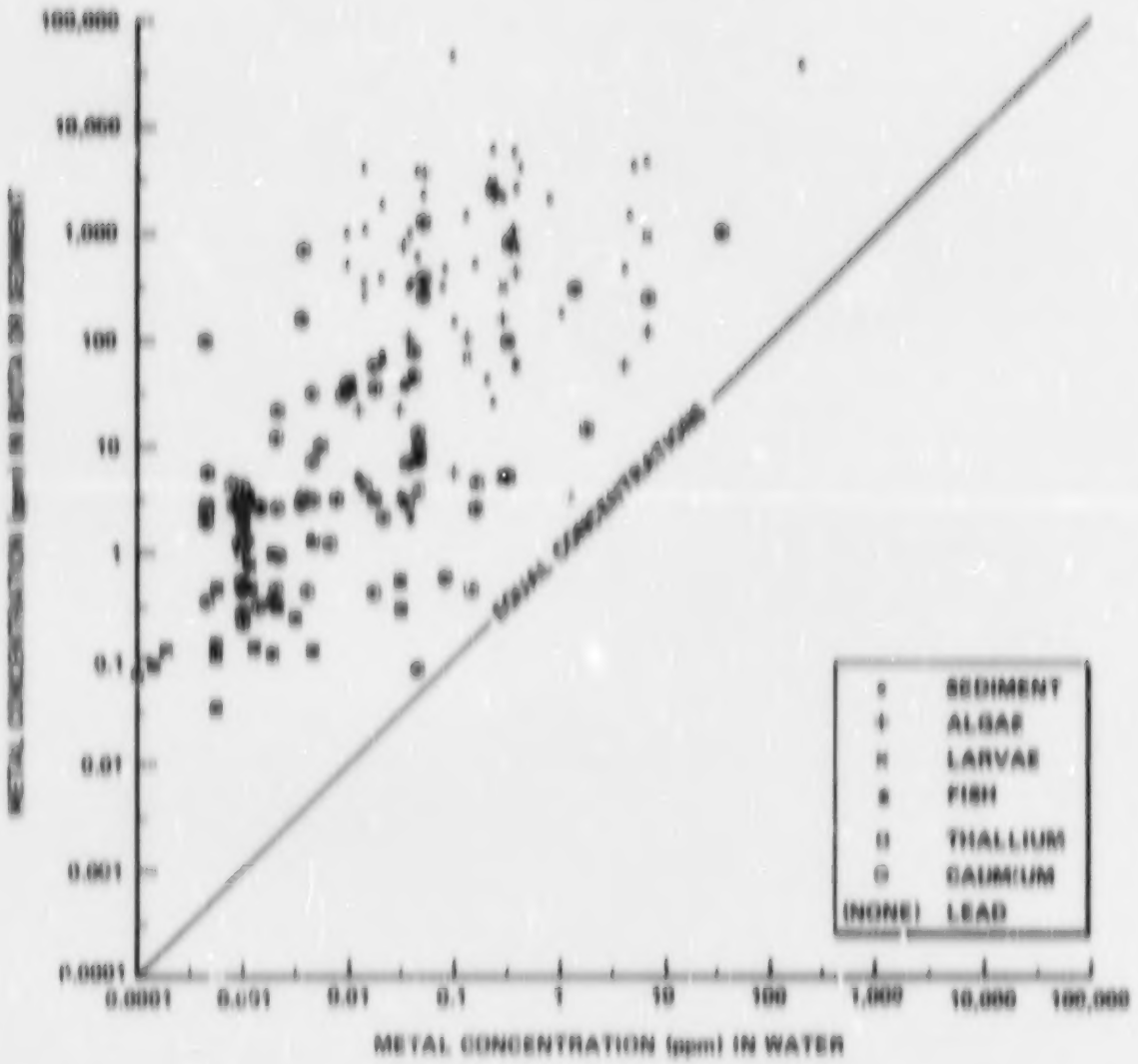


Figure 37. Concentration of the toxic metals thallium, cadmium, and lead in biota, sediment, and water.

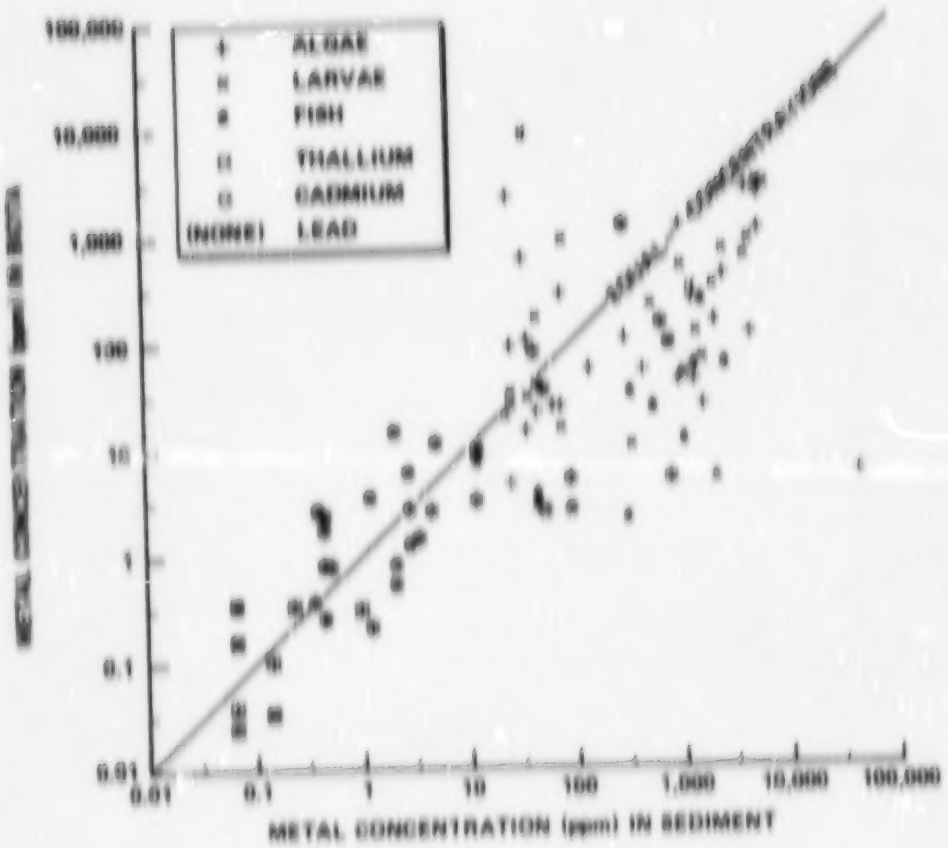


Figure 38. Concentration of the toxic metals thallium, cadmium, and lead in biota and sediment.

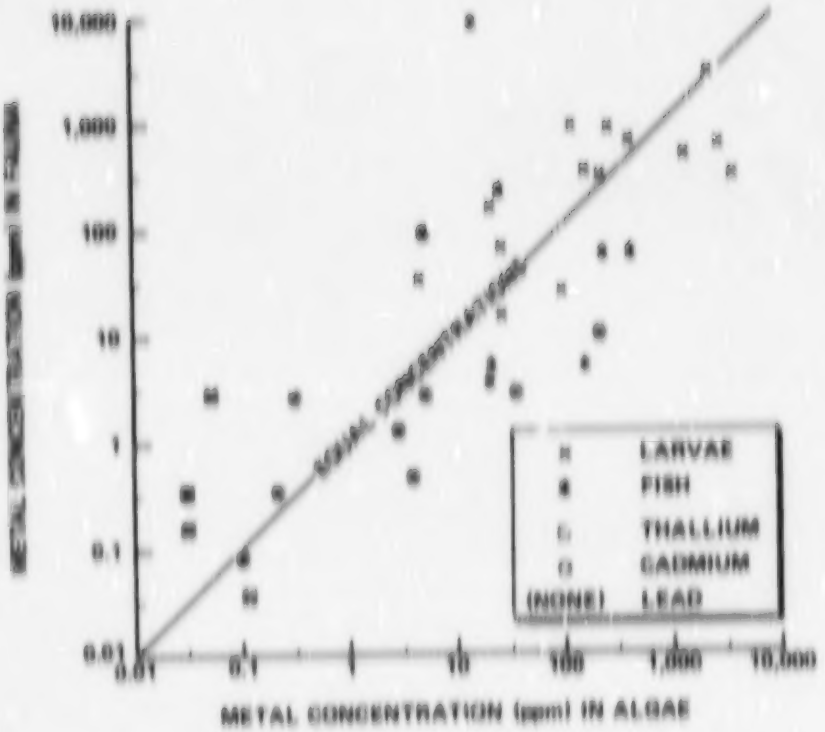


Figure 39. Concentration of the toxic metals thallium, cadmium, and lead in fauna and algae.

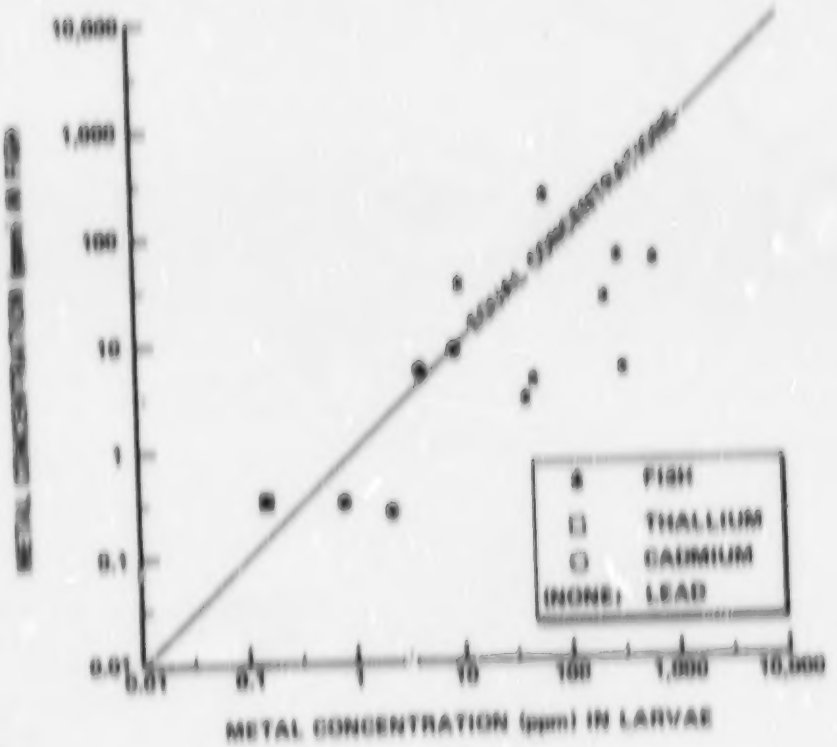


Figure 40. Concentration of the toxic metals thallium, cadmium, and lead in fish and larvae.

REFERENCES

1. Pinta, M. Detection and Determination of Trace Elements. Ann Arbor Science Publishers, 1971.

2. Hammer, D.I., et al. Trace-Metal Concentrations in Human Hair. In: Helena Valley, Montana, Area Environmental Pollution Study. U.S. Environmental Protection Agency, Office of Air Programs, Research Triangle Park, N.C., 1972. pp. 125-134.

3. Mink, L.L., R.E. Williams, and A.T. Wallace. Effect of Industrial and Domestic Effluents on the Water Quality of the Coeur d'Alene River Basin. Idaho Bureau of Mines and Geology, Pamphlet 149, Moscow, 1971.

4. Sargent, J.D. Thallium. In: Mineral Facts and Problems. U.S. Bureau of Mines Bulletin 556, 1952.

5. Gmelins. Handbuch der Chemie (Handbook of Chemistry). Anorganischen Chemie (Inorganic Chemistry), System 58. Section I: History, Occurrence and the Element, 1939 (revised 1962); Section II: Alloys and Compounds up to Thallium and Iodine, 1940 (revised 1962); and Section III: Concluding Compounds and Natural Isotopes, 1940 (revised 1962). Verlag Chemie GmbH, Leipzig (Germany).

6. Natusch, D.F.S., J.R. Wallace, and C.A. Evans. Toxic Trace Elements: Preferential Concentration in Respirable Particles. In: Science, 183, 1974. pp. 202-204.

7. Brown, A.S. Mineralisation in British Columbia and the Copper and Molybdenum Deposits. In: Canadian Inst. Mining Trans., 72, 1969. pp. 1-15.

8. Rex, R.W. and E.D. Goldberg. Insolubles. In: The Sea, Vol. I, Physical Oceanography, M.N. Hill, ed. Interscience Publishers, 1962.

9. Hager, S.W. Trace Metals in Oceanography of Nearshore Coastal Waters of the Northwest Pacific Relating to Possible Pollution. EPA WQO Grant 16070 EOE, 1971.

10. Merlini, M., C. Biglioccs, A. Berg, and G. Forni. Trends in Concentration of Heavy Metals in Organisms of a Mesotrophic Lake as Determined by Activation Analysis. In: Nuclear Techniques in Environmental Pollution. International Atomic Energy Agency, Vienna, 1971.

11. Feigl, F. Spot Tests. Vol. 1, Elsevier Publishing Co., 1954.

12. Stumm, W. and J.J. Morgan. Aquatic Chemistry. Wiley-Interscience, New York, 1970.

13. Rolf, G.L., J.W. Melin, and R.B. Ewing. Lead Pollution in a Watershed Ecosystem. Paper No. 931, 23rd ASAE Meeting at the University of Minnesota, 1972.

APPENDIX A

STUDY OF ALTERNATIVE SOLID-SAMPLE-PREPARATION METHODS

Sediment samples must be solubilized before analysis by atomic-absorption spectrophotometry, the analytical method used in this project. Sediments can be digested by utilizing a variety of acids (such as perchloric, hydrochloric, phosphoric, and sulfuric) but care must be taken not to volatilize the elements of interest (including thallium, lead, cadmium, zinc, and copper). Table A-1 gives data on volatilization losses of various heavy metals using the aforementioned acids.

Five methods for achieving the solution of metals from representative sediment and sludge samples were originally investigated. It was expected that an extraction technique which would provide reliable analysis of both of these sample types would also be applicable to those soils which would be collected throughout the program. The five sample-preparation procedures studied are:

(1) Pressure digestion--5 grams of sample were digested with 1.5 grams of perchloric acid ($HClO_4$) + 5.5 grams of nitric acid (HNO_3) in a closed bottle; stored overnight; and then cooled, diluted, and analyzed.

(2) Room-temperature extraction by mixed acids--5 grams of sample were extracted with 10 ml of nitric acid and 15 ml of hydrochloric acid (HCl) at room temperature, with a contact time of approximately 72 hours with occasional mixing.

(3) Boiling-acid extraction with resolubilization--0.5 gram of sample, 15 ml of hydrochloric acid, and 10 ml of nitric acid were heated and evaporated to dryness. The soluble residue was dissolved in 5 ml of hot hydrochloric acid and then diluted with water.

(4) Boiling-acid extraction--0.2 gram of sample, 15 ml of hydrochloric acid, and 5 ml of nitric acid were boiled 10 to 15 minutes, cooled, and diluted with water.

(5) Room-temperature extraction by nitric acid--5 grams of sample were extracted with 10 ml of nitric acid at room temperature for approximately 72 hours with occasional mixing.

TABLE A-1. SAMPLE DIGESTION WITH VARIOUS ACIDS

Volatilization of some metal compounds during digestion with perchloric, hydrochloric, sulfuric and phosphoric acids at 200-220°C (392-428°F).

Procedure 1. ($HClO_4$-HCl): 20 to 100 mg (0.3 to 1.5 grains) of the chloride are treated with 15 ml of 60% $HClO_4$; the temperature is raised to 200°C (392°F); 15 ml of HCl are slowly added (during 15 minutes) while the temperature is kept at 200-220°C (392-428° F).

Procedure 2. ($HClO_4$-H_3PO_4-HCl): same as procedure 1 except that 15 ml of $HClO_4$, 5 ml of 85% H_3PO_4, and HCl are used.

Procedure 3. (H_2SO_4-HCl): same as Procedure 1, $HClO_4$ being replaced by H_2SO_4 (d = 1.84).

The following elements are not volatilized by any of these procedures: Ag, alkali metals (Na, K, Rb, Cs), Al, Ba, Be, Ca, Cd, Co, Cu, Fe, Ga, Hf, In, Ir, Mg, Ni, Pb, Pd, Pt, rare earths, Rh, Si, Ta, Th, Ti, U, W, Zn, and Zr.

Element	Percent Volatilized		
	Procedure 1 $HClO_4$ - HCl	Procedure 2 $HClO_4$ - H_3PO_4 - HCl	Procedure 3 H_2SO_4 - HCl
As (III)	90	90	100
As (V)	5	5	5
Au	1	0.5	0.5
B	80	10	90
Br	0.1	0	0
Cr (III)	99.7	99.8	0
Ge	90	10	90
Hg (I, II)	75	75	75
Mn	0.1	0.02	0.02
Mo	3	0	5
Os	100	100	0
P	1	1	1
Re	100	80	90
Ru	99.5	100	0
Sb (III)	2	2	33
Sb (V)	2	0	2
Se (IV)	4	0.5	30
Se (VI)	4	0	20
Sn (II)	99.8	0	1
Sn (IV)	100	0	30
Te (IV)	0.5	0.1	0.1
Te (VI)	0.1	0.1	0.1
Tl (I, III)	1	1	1
V	0.5	0	0

Based on PINTA, 1971

One or two samples of each soil type were extracted by each technique to provide a measure of the reproducibility of the analytical results.

Results of the analysis are summarized in Table A-3, where an average for each of the two soil types and for each of the five sample-preparation procedures is also presented. The number of samples analyzed and the number used in determining the average values differ in several cases because those samples which were known to have significant experimental error were not included in the calculations of the averages or in determinations of the root-mean-square (rms) variations.

After evaluating the results of the five proposed preparation techniques, a general method for solid-sample preparation was developed which most closely allied those two methods which seemed to yield the highest concentration of metals (i.e., Procedure (2) and Procedure (5) above). The final sediment-preparation method, discussed in the text of Section 5 under Sample Preparation, consisted of a mixed-acid digestion at room temperature for 24 hours.

As discussed in Section 5, sulfide precipitation was not utilized as a method for sample preparation because of its failure to yield detectable thallium concentrations below 0.5 ppm. Apparently, there are interferences remaining in solution after precipitation which completely quench the thallium signal when the heated graphite atomizer is used for analysis. Table A-5 gives the details of the sulfide preparation procedure. Although this method remains a viable choice for preparation of those samples with high metal concentrations, it was not applicable for this study because of the high level of sensitivity for thallium which was desired.

The organic-complexation method for thallium (Section 5) resulted from an intense effort throughout the program to develop a sample-preparation procedure which would consistently yield reliable thallium levels in a variety of sample types--especially, at low concentrations.

The organic-complexation method fulfilled this requirement. Analytical results of tests run on selected water and sediment samples are shown in Table 4 (Section 5). Of particular interest in this table is the high rate of recovery of the thallium spike--notably, in the water samples. The rate of spike recovery in the sediment samples is somewhat less, as can be seen from the table. This may be due to the large amounts of other metals present that also complex with the DDC and reduce the DDC-to-thallium ratio, thereby leaving the thallium with little DDC available for complexation. The reduced signal may also be due to the large amounts of other extracted metals interfering with thallium.

As previously mentioned, this method yielded the most consistent results and was, therefore, utilized throughout the program for analyzing samples for the presence of thallium.

TABLE A-3. ANALYTIC RESULTS (in ppm) OF SAMPLE PREPARATION TRIALS

	Cd	Cu	Pb	Tl	Zn
SOIL TYPE A					
Average (Mean)	194	22,000	2,661	5.1	1,720
Procedure 1 (2 samples)	180	23,000	1,170	1.7	2,060
Procedure 2 (2 samples)	200	21,000	3,033	3.5	1,900
Procedure 3 (2 samples)	1L.5	22,000	3,016	ND	1,650
Procedure 4 (2 samples)	183	23,000	3,140	ND	1,600
Procedure 5 (2 samples)	200	20,000	2,660	2.8	1,800
No. of Samples	10	10	10	8	10
No. of Samples in Average	7	7	7	4	7
No. of Measurements in Average	7	14	12	8	10
Rms Deviation of Measurements	18.4	1,000	256	0.74	130
Rms Deviations of Sample Averages	18.4	1,500	219	0.75	125
SOIL TYPE B					
Average (Mean)	66	50,000	1,400	7.0	418
Procedure 1 (2 samples)	67	50,000	1,300	6.2	405
Procedure 2 (2 samples)	60	51,000	1,480	6.2	410
Procedure 3 (1 sample)	67	48,000	1,460	ND	479
Procedure 4 (1 sample)	68	53,000	1,390	ND	405
Procedure 5 (2 samples)	66	48,000	1,410	7.4	380
No. of Samples	6	6	6	6	6
No. of Samples in Average	6	6	6	6	6
No. of Measurements in Average	8	10	10	8	10
Rms Deviation of Measurements	4.3	3,800	103	1.3	59
Rms Deviation of Sample Averages	4.3	2,500	74	1.4	33

ND = Not determinable (<0.001 ppm)

TABLE A-3. SULFIDE PRECIPITATION PROCEDURE

1. Exactly 10.0 ml of sample is acidified with 1 ml of HNO_3 and 1 ml of HCl.
2. The pH is then adjusted to 12 with 2.5 M sodium hydroxide.
3. 0.5 g of Na_2S, dissolved in 1 ml of water, is added.
4. When no observable precipitate forms, 1 ml of 1000 ppm Zn and 1 ml of 1000 ppm Pb are added.
5. The resulting solution is filtered through a millipore HWAG 0.45 micrometer filter.
6. The precipitate is redissolved in 5 ml of concentrated nitric acid and made up to 10 ml in a volumetric flask with distilled water.
7. Sample is then ready for subsequent analysis.